Anion Exchange Adsorption of Some Metals from Mixed Solvents[1]

By Yukichi Yoshino and Yoshimi Kurimura

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Recently K.A. Kraus and his coworkers[2] have carried out an extensive study on anion exchange adsorption of a number of metallic elements from a hydrochloric acid solution and its related media.

In the present paper, anion exchange adsorption data for zinc(II) and copper (II) from organic solvent—hydrochloric acid mixtures are described and the effect of the addition of the organic solvents are discussed.

Experimental

Materials. — The anion exchanger used was polystyrene-divinylbenzene quarternary amine resin Dowex 1-X8, supplied as beads of 50–100 mesh. The resin was cycled twice with 1N sodium hydroxide and then with 1N hydrochloric acid; after complete conversion into the chloride form it was thoroughly washed with deionized water. The chloride resin was dried to constant weight in a desiccator over silica-gel. The resin thus obtained was found to have a capacity of 3.29 milliequiv. per gram. Dowex 1-X4 resin which was conditioned and dried in the same manner had a capacity of 3.15 milliequiv. per gram.

The organic solvents such as methanol, ethanol, *n*-propanol and acetone were all of "JIS"* first class grade and purified by distillation. Concentrated hydrochloric acid of "JIS" special class quality was used without further purification. Dilute hydrochloric acid was prepared from distillate of azeotropic mixture. Other chemicals are all of "JIS" special class grade and purified by distillation or recrystallization when necessary.

The zinc tracer** was ^{65}Zn ($T_{1/2}$=250 days). An aliquot of the hydrochloric acid solution was dried up and preserved as 0.1M perchloric acid solution. The absorption characteristic and cation anion exchange chromatographic behavior showed that the tracer was of satisfactory purity.

Measurement of Adsorbability. — The adsorbability of the elements was measured by the equilibrium method and the results were described in terms of distribution coefficient K_d defined as amount of element per gram resin/amount per milliliter solution. In the measurement of K_d of zinc(II), a known weight of dry resin was added to 30 or 40 ml. of mixed solvents and was left overnight until swelling equilibrium was attained. Then 1 ml. of the tracer solution was added and the resulting solution was shaken mechanically in a thermostat at 25±0.1° for three hours. The supernatant solution was pipetted using filter-tubes packed with glass-wool and the radioactivity was measured with a Kobe Kogyo's dipping type G.M. counter of scale-of-64. Factors such as the geometry and the self-absorption were kept as constant as possible. From the resultant decrease in radioactivity of the solution, the values of distribution coefficients were calculated. Preliminary experiments revealed that the constancy of K_d values was attained when the loading of the resin was kept less than ca. 0.5% of resin capacity.

The distribution coefficient of copper(II) was estimated in the same manner as in the case of zinc(II) except that the decrease in the concentration was measured photometrically using carbamate method[3] (436 mμ). Extinction and spectra were measured by means of a Hitachi's EPU-2 spectrophotometer. The amount of copper was taken so as to be less than 1% loading with respect to the resin capacity.

The chloride ion concentration was determined by titration with 0.1 or 0.01N silver nitrate solution using Goodall and Mellor's dead-stop method[4].

Results and Discussion

Adsorption of Zinc(II) from Mixed Solvents.—In Fig. 1, distribution coefficients of zinc(II) in hydrochloric solution containing 30 and 60% (v/v) methanol were plotted against the molarity of hydrochloric acid (curve 2 and 3). For comparison, the adsorbability in a hydrochloric acid solution was shown by curve 1, which seems to conform very closely to Kraus's[2].

1) Presented at the Symposium on the Complex Compound Chemistry, October 27, 1956, Tokyo.

2) For example, K. A. Kraus and G. E. Moore, *J. Am. Chem. Soc.*, **75**, 1460 (1953); K. A. Kraus, F. Nelson and G. W. Smith, *J. Phys. Chem.*, **58**, 11 (1954); K. A. Kraus and F. Nelson, Peaceful Uses of Atomic Energy, Proceedings of the International Conference in Geneva, Vol. VII, 113 (1955) United Nations.

* Japan Industrial Standard.

** Zn-65 (P-1) obtained from U. S. Atomic Energy Commission. The specific activity was 261 mC./g. Zn. on Dec. 23, 1955.

3) E. B. Sandell, "Colorimetric Determination of Traces of Metals" 304 (1950) Interscience Publishers, Inc., New York.

4) R. R. Goodall and N. Mellor, *Anal. Chim. Acta*, **5**, 373 (1952).

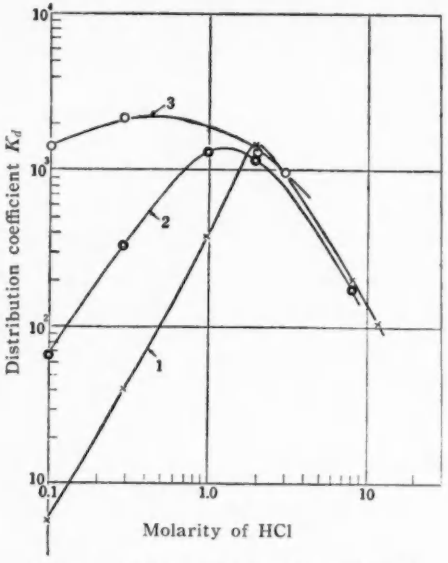


Fig. 1. Anion exchange adsorption of Zn(II).
1. in HCl solution
2. in HCl-30% (v/v) methanol mixture
3. in HCl-60% (v/v) methanol mixture

It is clear that the addition of methanol increases the adsorbability of zinc (II) in the range of lower hydrochloric acid concentrations, i.e. less than 2 M, while in a higher concentration, the effect is not clear. An interesting feature of the results is that the more the concentration of the hydrochloric acid is decreased, the more pronounced the effect and, at the same time, adsorption maxima shift to lower hydrochloric acid concentration.

In order to see the details of the relation between the adsorbability and the concentration of the organic solvent, the distribution coefficient of zinc(II) in various mixed solvents containing methanol, ethanol, *n*-propanol or acetone was examined at constant hydrochloric acid concentration i.e. 0.1 M. The results were summarized in Fig. 2.

The addition of these materials was found to be likewise effective for increasing of the adsorbability of zinc(II). In general the straight line relation between the logarithm of distribution coefficient and the concentration of organic solvents was observed in the range up to at least ca. 60 %. The order of the effect to increase the adsorbability of zinc(II) on the weight bases is:

Acetone≧ethanol>methanol>n-propanol

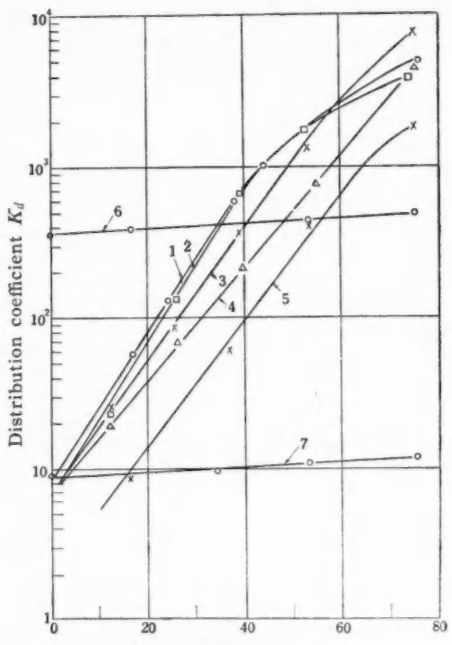


Fig. 2. Effects of various organic solvents on the anion exchange adsorption of Zn(II) in 0.1 M HCl.
1. Acetone
2. Ethanol
3. Methanol
4. *n*-Propanol
5. Methanol (Dowex 1-X4)
6. RNO_3+Cl^-, $\mu=0.003$, (NaCl) Methanol
7. RNO_3+Cl^-, $\mu=0.1$, (KNO_3) Methanol

The experimental data using less cross-linked resin (Dowex 1-X4) in methanol-hydrochloric acid media were also plotted in Fig. 1 (curve 5). The result is very similar to those of 8 % cross-linked resin except that the lower K_d values were obtained.

In the cation exchange equilibria involving alkali and alkaline earth metal ions, Sakaki and Kakihana[5] had previously pointed out that the effect of addition of an alcohol depends, as a first approximation, on the dielectric constants of mixed solvents and is indifferent to the kind of alcohol added, i.e. methanol or ethanol. In the authors' experiments, this relation

5) T. Sakaki and H. Kakihana, *Kagaku (Science)*, **23**, 71 (1953).
T. Sakaki, This Bulletin, **28**, 217, 220 (1955).

was also proved to hold in the media containing methanol and ethanol but the relation no longer holds in cases of other solvents as is seen in Fig. 3.

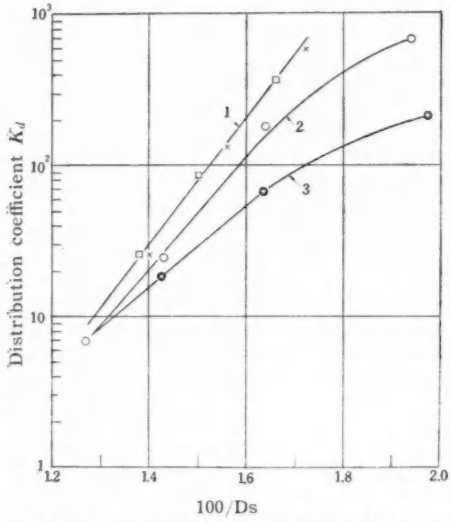


Fig. 3. Relation between K_d of Zn(II) and dielectric constants of solutions in at 0.1 M HCl.
1. Methanol (-×-×-), Ethanol (-□-□-)
2. Acetone
3. *n*-Propanol

Then as a base of comparison, a simple ion, i.e. a chloride ion was equilibrated to the nitrate resin in methanol-water mixtures (curves 6 and 7 in Fig. 2). In this case, the solvent effect was found to be slight as compared with the case described above.

Kraus[2] suggested that in the elements which show adsorption functions with maxima such as zinc(II), cadmium(II) and gallium(III), the portion of increasing absorbability with increasing hydrochloric acid concentrations is due to the formation of the negatively charged complexes and that the maxima occur at approximately those hydrochloric acid concentrations where the negatively charged complexes become predominant. In view of this, all the experimental data described above seem to imply that the addition of organic solvents favors the dehydration of aquated zinc ions and consequently favors the stepwise formation of negatively charged chloro-complexes as may be expressed by the following set of equations,

$$Zn(H_2O)_4^{2+}+Cl^- \longrightarrow ZnCl(H_2O)_3^+ + H_2O$$
$$ZnCl(H_2O)_3^+ + Cl^- \longrightarrow ZnCl_2(H_2O)_2 + H_2O$$
$$ZnCl_2(H_2O)_2 + Cl^- \longrightarrow ZnCl_3(H_2O)^- + H_2O$$
$$ZnCl_3(H_2O)^- + Cl^- \longrightarrow ZnCl_4^{2-} + H_2O$$

Adsorption of Copper(II) from Mixed Solvents.—According to Kraus[2], the adsorbability of copper(II) from hydrochloric acid solution is relatively weak, showing a flat maximum in ca. 7 M hydrochloric acid (the elution constant E=ca. 0.1). The results of our measurements up to 8 M hydrochloric acid are shown by curve 1 in Fig. 4, which seems to be in fairly good agreement with Kraus's results. The effect of addition of methanol to this system is summarized in Fig. 4, (curves 2, 3, 4).

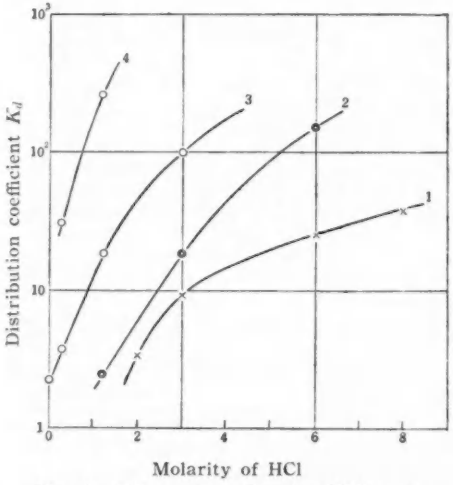
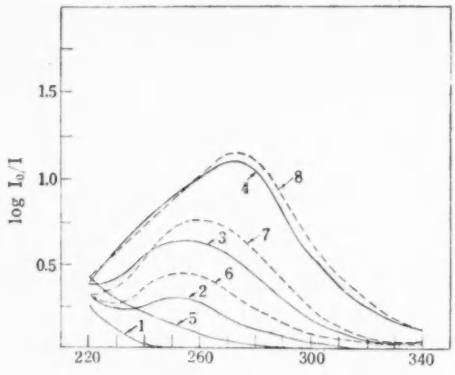


Fig. 4. Effect of methanol addition on the anion exchange adsorbability of Cu(II).
1. HCl only
2. 30% (v/v) methanol
3. 60% (v/v) methanol
4. 80% (v/v) methanol

In comparison to the case of zinc(II), the increase in the adsorbability of copper(II) in the presence of methanol was observed up to higher hydrochloric acid concentrations: This fact seems to suggest that the negatively charged complexes of Cu(II) are not completely formed throughout the range of hydrochloric acid concentration studied.

This may also be understood by the adsorption spectra of the copper(II) solution in the ultraviolet region*. As is seen

* The absorption spectra of chloro-complexes of zinc (II) in the ultraviolet region could be detected only in the range of higher zinc(II) concentration (more than 1 M) where the constancy of K_d can no longer hold and the experimental results are not comparable with each other.



Wave length, mμ

Fig. 5. Absorption spectra of Cu(II) in HCl or HCl-methanol mixtures.
$Cu(ClO_4)_2$, 4×10^{-4} M, Cell, 10 mm
1. in water
2. 1.2 M HCl
3. 3.0 M HCl
4. 5.0 M HCl
5. 80% (v/v) methanol
6. 1.2 M HCl-30% (v/v) methanol
7. 1.2 M HCl-60% (v/v) methanol
8. 1.2 M HCl-80% (v/v) methanol

from the curves 6, 7 and 8 in Fig. 5, the increase of methanol concentration in the 1.17 M hydrochloric acid solution of copper (II) resulted in the increasing formation of chloro-complexes in just the same manner as in increasing the concentration of hydrochloric acid in the absence of methanol (curves 2, 3, 4).

Katzin and Gebert[6] have found the adsorption of various inorganic salts onto anion exchange resin from their solution in acetone and suggested as a possible mechanism that the salts of transition elements might be adsorbed as complex anions. On the other hand, Davies and Owen[7] have postulated the possibility of the passage of the salts from acetone solutions into the resin phase from the standpoint of unequal partition of the solvents between both phases.

However, it was ascertained that tracer scale calcium chloride ($^{45}CaCl_2$*) in 0.1 M hydrochloric acid-methanol solution showed only negligible adsorption in the range less than 80% methanol. Therefore, under the conditions of our experiments, where the content of water is relatively high, the pronounced effect of increase in the adsorbability of zinc(II) and copper(II) might, if not completely, be explained by the dehydration effect of organic solvents added.

The remarkable rise in the adsorbability of the elements in the regions of relatively low hydrochloric acid concentrations may be of great use in the anion exchange separation of the elements which show only slight adsorption in dilute hydrochloric acid solutions and also in their rapid determination using the methods other than radiometry, e.g., complexometric titration[8].

Summary

1) It was found that the addition of some organic solvents such as methanol, ethanol, *n*-propanol and acetone to the hydrochloric acid solution of zinc(II) and copper(II) increases the anion exchange adsorption of the elements in the range of relatively low hydrochloric acid concentrations (less than 2 M). In the 0.1 M hydrochloric acid solution, the straight line relation between log K_d and concentration of organic solvent was observed up to ca. 60 %.

2) In the case of copper(II), this effect of increasing the adsorbability was observed up to higher hydrochloric acid concentrations i.e., at least 8 M, which seems to reflect that the adsorption maximum occurs at a higher hydrochloric acid concentration than in the case of Zn(II).

3) It was suggested that these solvent effects may be, as a first approximation, explained by the increase in the formation of negatively charged chloride complexes of the metals as a consequence of the decrease in the tendency for solvation of metallic ions in mixed solvents.

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Department of Chemistry, The College of General Education, The University of Tokyo, Komaba, Meguro-ku, Tokyo

6) L. I. Katzin and E. Gebert, *J. Am. Chem. Soc.*, **75**, 801 (1953).

* Ca-45 (P-2) ($T_{1/2}$=164 days), obtained from Atomic Energy Commission of U. S. A.. Its specific activity was 14.59 mC./g. solid on Feb. 10, 1955.

7) C. W. Davies and B. D. R. Owen, *J. Chem. Soc.*, **1956**, 1676.

8) For example, G. Schwarzenbach, "Die komplexometrische Titration" 2nd Ed. (1956). Ferdinand Enke Verlag, Stuttgart.

Photometric Determination of Thallium with Rhodamine B

By Hiroshi ONISHI

(Received January 28, 1957)

In an earlier communication[1] a photometric method for the determination of thallium with rhodamine B was briefly described. The purpose of the present paper is to treat the same subject in greater detail. The extraction with dithizone in chloroform was adopted for the separation of thallium from other elements. Although the recoveries of thallium are slightly low, the proposed method may be of general use for the determination of traces of this element.

Experimental

Apparatus. Absorbance measurements were made with Hitachi Models EPB-U and EPV-2 spectrophotometers, using 1-cm. cells. At a later stage of the present investigation, the EPV-2 spectrophotometer was exclusively used.

Solutions. *Ammonium citrate*, 20 g. of $(NH_4)_2HC_6H_5O_7$ in 100 ml. of water.

Potassium cyanide, 10 g. in 100 ml. of water.

Hydroxylamine hydrochloride, 20 g. in 100 ml. of water.

Dithizone, 0.50 g. in 500 ml. of redistilled chloroform. Purify it freshly before use by washing the dithizone solution three times with 1 : 100 nitric acid, and then three times with 1 : 1000 ammonium hydroxide.

Rhodamine B, 0.20 g. in 100 ml. of water.

Standard thallium solution. Dissolve 0.124 g. of pure Tl_2SO_4 in 100 ml. of 0.5 N sulfuric acid. From this stock solution (1.00 mg. Tl per ml.) prepare a working standard solution containing 0.010 mg. (10 μg.) of Tl per ml. by diluting with 0.5 N sulfuric acid. This solution can be kept for at least two weeks.

Procedure. Transfer the sample solution (1–10 μg. Tl in a volume of about 30 ml.), which may conveniently be about 0.1 N in sulfuric acid, to a beaker and add 10 ml. of ammonium citrate solution. Add a few drops of thymol blue indicator solution and 1 : 1 ammonium hydroxide until the color turns blue. If, because of the presence of heavy metals, no color change can be definitely observed, adjust pH of the solution to 10 by the use of a pH meter.

Add 15 ml. of potassium cyanide solution and after a few minutes add 5 ml. of hydroxylamine hydrochloride and 3 ml. of 1 : 1 ammonium hydroxide, mix, and let stand for a few minutes. If the color of the solution fades to a blue color, or nearly so, transfer the solution to a separatory funnel. If the deep red color produced does not fade appreciably upon standing for a few minutes, heat the solution on a water bath for 3–5 minutes, and then cool with water. Transfer the solution to a separatory funnel and wash the beaker with 10 ml. of 1 : 1000 ammonium hydroxide.

Extraction of thallium. Shake the solution for one minute with 10 ml. of dithizone solution. When the layers have separated, drain off the chloroform phase into another separatory funnel. Extract further the aqueous phase with two 10 ml. portions of dithizone solution. Combine the extracts and discard the aqueous layer. Wash the extracts with 10–20 ml. of 1 : 1000 ammonium hydroxide followed by 10–20 ml. of water. Drain the chloroform phase into another separatory funnel and shake vigorously for one minute with 10 ml. of 1 : 100 nitric acid to extract thallium. Draw off the chloroform into another separatory funnel and extract with another portion (5–10 ml.) of nitric acid. Drain off and discard the chloroform layer and transfer the aqueous extracts to a 50 ml. beaker containing 0.50 ml. of 1 : 5 sulfuric acid, rinse the separatory funnels with 1–2 ml. of 1 : 100 nitric acid and evaporate to fumes. When the sulfuric acid residue shows a brown color due to the presence of organic matter, add about 20 mg. of ammonium persulfate and allow to fume for a few minutes. Repeat this step until a colorless solution is obtained.

Cool, add 5.0 ml. of 2.0 N hydrochloric acid and 1.0 ml. of saturated bromine water. Heat near the boiling point and stop heating when the color due to bromine has disappeared. Cool to room temperature, transfer the solution to a 10 ml. volumetric flask and dilute to the mark with 2.0 N hydrochloric acid.

Determination of thallium. Transfer the solution to a separatory funnel as completely as possible, add 1.0 ml. of rhodamine B solution and mix. Without undue delay add 10.0 ml. of pure benzene and shake for one minute. When the two phases have separated, drain off the aqueous phase, transfer the benzene layer into a centrifuge tube, and centrifuge for about 2 minutes. Measure the absorbance of the clear benzene extract at 560 mμ, using benzene as the reference solution.

Establish the standard curve by taking, for example, 0, 2, 4, 7, and 10 μg. of thallium into beakers respectively, adding 0.50 ml. of 1 : 5 sulfuric acid, 5.0 ml. of 2.0 N hydrochloric acid, 1.0 ml. of bromine water, and proceeding as described above. Run a blank through the entire procedure.

1) H. Onishi, This Bulletin, **29**, 945 (1956).

As the recoveries of thallium are slightly low, a correction of +10 per cent. is probably advisable. See **Discussion.**

Results and Discussion

Photometric Determination of Thallium. Bromine is a very satisfactory reagent to oxidize univalent thallium to tervalent. Excess of bromine can be easily removed by heating. The use of ammonium persulfate to destroy organic matter in the residue from the evaporation of nitric acid extract gave an opportunity to find another suitable oxidizing agent for thallium (Fig. 1). Oxidation with ammonium persulfate was effected in the following way. A known amount of thallium and 0.50 ml. of 1:5 sulfuric acid in a 50 ml. beaker were heated on a sand bath to fumes, about 20 mg. of ammonium persulfate was added and heated while whirling the beaker. After cooling

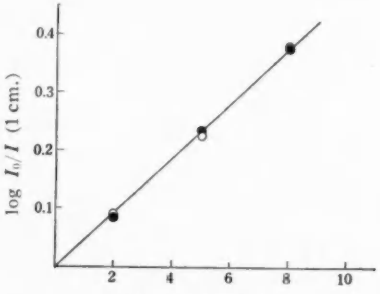

Fig. 1. Oxidation of thallium (I) with ammonium persulfate and bromine.
●: ammonium persulfate
○: bromine
1.6 N HCl, Hitachi EPV-2 spectrophotometer, 560 mμ.

the same amount of persulfate was again added and evaporated to fumes. A few drops of water were added and evaporated to fumes. Ten ml. of 2.0 N hydrochloric acid was added followed by rhodamine B-benzene extraction. When ammonium persulfate is left undecomposed and brought to rhodamine B extraction, rhodamine B is oxidized and erratic results are obtained. The above procedure eliminates this defect. However, that procedure appeared to be slightly more troublesome, so the step of bromine oxidation has been retained in the proposed procedure. Excess of persulfate was decomposed during the treatment with bromine. Tervalent thallium obtained by either oxidation procedure was stable for at least one hour. Several other reagents were tried to oxidize thallium, but it was difficult to remove excess of any reagent without affecting the thallium. An attempt to remove the excess with an excess of rhodamine B was unsuccessful.

The absorptions pectrum (in benzene) of rhodamine B chlorothallate, which is considered to be the compound of thallium (III) with rhodamine B, is shown in Fig. 2. Correction is applied to the reagent blank. The absorption peak is found at

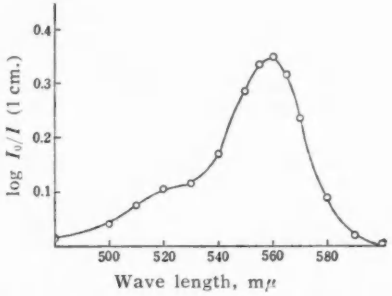

Fig. 2. Absorption spectrum of rhodamine B chlorothallate in benzene (0.8 p.p.m. Tl in benzene). Hitachi EPB-U spectrophotometer.

560 mμ. It is of interest to compare this peak with that of other compounds of the type $(RH)M^{III}Cl_4$ (R=rhodamine B). Rhodamine B chloroantimonate, $(RH)SbCl_6$, shows the maximum at 564 mμ, and rhodamine B chlorogallate at about 565 mμ[2]. The maximum of RH^+ in water was found to be at 556 mμ[3]. It does not seem that the absorption spectra of $(RH)FeCl_4$ and $(RH)AuCl_4$ have been described. At any rate, all three known compounds in benzene show the absorption peak at about 560 mμ. Moreover, the shapes of their absorption spectra are quite similar. The molar absorptivities of thallium, gallium, and antimony are 96,000*, 60,000, and 100,000 respectively. The value for RH^+ in water is 110,000[3]. It may be concluded that the deep coloration of these compounds is mainly due to RH^+ species.

The extractability of rhodamine B

2) H. Onishi and E. B. Sandell, *Anal. Chim. Acta*, **13**, 159 (1955).
3) R. W. Ramette and E. B. Sandell, *J. Am. Chem. Soc.*, **78**, 4872 (1956).
* A value of 87,000 was given in the previous paper. The EPB-U spectrophotometer gave low absorptivities.

chlorothallate as a function of hydrochloric acid concentration is shown in Fig. 3. The concentration was calculated and

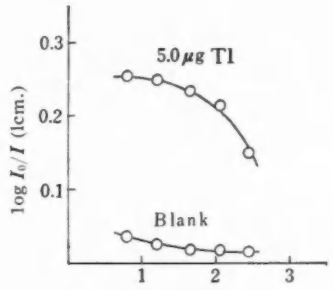

Fig. 3. Extractability of rhodamine B chlorothallate as a function of hydrochloric acid concentration. Hitachi EPV-2 spectrophotometer, 560 mμ.

correction was not made for evaporation loss during the treatment with bromine. A half ml. of 1 : 5 sulfuric acid was present in each case. In the figure 1.6 N corresponds to the concentration of hydrochloric acid in the proposed procedure.

It is seen that the acid concentration must be kept constant to get reproducible results. Consequently heating in bromine treatment must always be done in the same way. At each hydrochloric acid concentration studied, i.e., 0.8, 1.2, 1.6, 2.0, and 2.5 N, the absorbance was proportional to thallium concentration in the range 0.1 to at least 1 p.p.m. (based on the amount of thallium present originally in the aqueous phase).

The effect of the concentration of rhodamine B (reagent grade, Katayama Chemical Works, Osaka) on the absorbance of rhodamine B chlorothallate in benzene is shown in Fig. 4. Corrections for reagent blanks were made. In all cases the hydrochloric acid concentration was maintained at 2.0 N (slightly higher than the acidity recommended for **Procedure**). The absorbance increases very slightly with an increase in the concentration of rhodamine B, and the reagent blank also increases slightly. In the present investigation, about 4×10^{-4} M in rhodamine B (or 1.0 ml. of 0.20 % rhodamine B solution) was adopted. At the concentration the reagent blank was in the range 0.010~0.020 against pure benzene. The extraction coefficient for 1.6 N hydrochloric acid and 0.00038 M rhodamine B in the aqueous phase is

$$\frac{[Tl]_{benzene}}{[Tl]_{H_2O}}=13 \quad \text{(from Table 1)}$$

This constant is independent of the thallium concentration in the range investigated. Consequently the volume of the aqueous phase must be maintained constant for reproducibility.

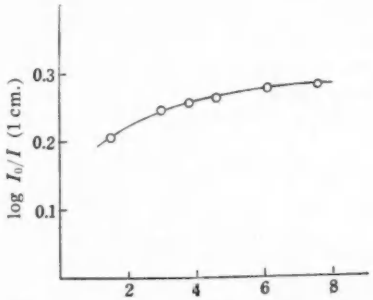

Fig. 4. Effect of rhodamine B concentration on absorbance of rhodamine B chlorothallate. 6.0 μg. Tl taken, 2.0 N HCl, Hitachi EPB-U spectrophotometer.

TABLE I

EXTRACTABILITY OF RHODAMINE B CHLOROTHALLATE WITH BENZENE

[Aqueous phase (11 ml.) 1.6 N in HCl and 0.00038 M in rhodamine B; 10 ml. benzene; temperature 18–20°C]

Tl present, μg.	4.0	6.0	10.0
Absorbance of first extract (560 mμ)	0.175	0.262	0.435
Absorbance of second extract (10 ml.)	0.013	0.022	0.033
Extraction coefficient*	14.5	12	13.5

* Average is 13.

The absorbance of the benzene extract does not change for at least one hour (Table II).

TABLE II

STABILITY OF BENZENE EXTRACT

Time after extraction, min.	I	II	III
5	0.221	0.366	0.420
30	0.218	0.364	0.419
60	0.217	0.363	0.427

Most of the colorimetric methods available at the present time are indirect. The iodine method by Haddock[4] was used for the determination of 10–200 μg. of thallium after extraction with dithizone. Thallium

4) L. A. Haddock, *Analyst*, **60**, 394 (1935).

TABLE III

DETERMINATION OF THALLIUM WITH RHODAMINE B AFTER DITHIZONE-CHLOROFORM EXTRACTION

Addition	Tl taken, μg.	Tl found, μg.*		Tl recovered, %	
		Single HNO_3 extraction	Double HNO_3 extraction	Single HNO_3 extraction	Double HNO_3 extraction
none	2.2	1.9**, 2.1**		86**, 95**	
none	5.0	5.0**, 5.2**, 4.2, 4.5	4.5, 4.7	100**, 104**, 84, 90	90, 94
none	5.5	5.7**, 5.0**, 5.9**, 5.5**		104**, 91**, 107**, 100**	
none	8.7	7.8**, 7.8**		90**, 90**	
10 mg. Cu, 10 mg. Ni	5.0	4.6		92	
1.0 mg. Ag, 1.1 mg. Pt	5.0	4.2		84	
1.2 mg. Au(III), 1.0 mg. Sb(III)	5.0	4.9, 4.7		98, 94	
10 mg. Zn, 10 mg. Hg(II)	5.0		4.7		94
40 mg. Al, 1.1 mg. Ga	5.0	4.4		88	
1.1 mg. In	5.0		4.7		94
1.0 mg. Ge(IV), 1.0 mg. Sn(II)	5.0		4.6		92
1.0 mg. Pb	5.0		4.5		90
10 mg. P(as KH_2PO_4), 1.0 mg. As(III)	5.0		4.6		92
1.0 mg. Bi	5.0		4.6		92
1.0 mg. Mo(VI), 1.0 mg. W(VI)	5.0		4.4		88
50 mg. Fe(III)	5.0	4.2, 4.2		84, 84	
100 mg. Fe(III)	2.0	1.7		85	
100 mg. Fe(III)	5.0	4.3, 4.1	4.6, 4.5	86, 82	92, 90
100 mg. Fe(III)	8.0	6.6		83	

* Correction applied for blank: 0.0 μg. with no addition, and with Cu+Ni, Ge+Sn, Pb, P+As, Mo+W, and Fe; 0.1 μg. with Au+Sb, Zn+Hg, and Al+Ga; 0.2 μg. with Ag+Pt; 0.3 μg. with In; and 0.4 μg. with Bi.

** $NH_2OH \cdot HCl$ added before KCN, ammonium citrate, and NH_4OH.

dithizonate in chloroform was evaporated to dryness followed by oxidation with hydrogen peroxide.

Berg et al.[5] described the determination with thionalide. Among the newer colorimetric methods, the *p*-phenetidine method[6] has a sensitivity of about 0.3 μg. Tl/cm^2 corresponding to $\log I_0/I=0.001$, or a molar absorptivity of 6,000. Iron and gold interfere with the determination. Neither the dibenzyldithiocarbamate[7] nor thallium hydroxide[8] methods are sensitive; the molar absorptivity of the former is 1,340 and that of the latter 561. Colorimetric determination of cobalt with nitroso-R salt after precipitation of $[Co(NH_3)_6]TlCl_6$ gave the amount of thallium indirectly[9]. This precipitate was also utilized for the radiometric determination of thallium by means of radioactive cobalt[10,11]. This method and also the radioactivation method[12] appear to be as sensitive as the rhodamine B method described here.

Separation of Thallium. Metals that must be separated because of more or less sensitive color reaction with rhodamine B are antimony, gold, iron, and tungsten. As much as 1 mg. of gallium in 2 N hydrochloric acid does not give any appreciable color and does not interfere with the determination of thallium. As a method of separation of thallium, the extraction with dithizone is thought to be superior to the ether extraction of chloride or bromide. By the ether extraction gold will be extracted with thallium and it must be separated by an appropriate method, e.g., reduction to metal and filtration.

5) R. Berg, E. S. Fahrenkamp, and W. Roebling, *Mikrochemie* (Molisch Festschrift), 42 (1936).
6) S. Iijima and Y. Kamemoto, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **75**, 1294 (1954).
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8) V. K. Zolutukhin and A. S. Molotkova, *Zhur. Anal. Khim.*, **11**, 248 (1956).
9) T. Nozaki, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **77**, 493 (1956).
10) T. Ishimori, This Bulletin, **26**, 336 (1953).
11) T. Ishimori and Y. Takashima, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **76**, 858 (1955).
12) C. J. Delbecq, L. E. Glendenin and P. H. Yuster, *Anal. Chem.*, **25**, 350 (1953).

Dithizone extraction of thallium has been investigated by several workers. It is well known that the only metals reacting with dithizone in a slightly basic medium containing cyanide are bismuth, lead, thallium, and tin. Except thallium, none of these reacts with rhodamine B. Recently Ishimori[10,11] determined traces of thallium radiochemically after its separation with dithizone. His results showed that the recoveries of thallium were 46 to 67%, and the loss was found to occur when thallium was extracted with dilute nitric acid from dithizone-chloroform solution. Evaporation of dithizone-chloroform extract followed by oxidative decomposition of organic matter will undoubtedly bring better recoveries. This method is, however, not very convenient. In the present work, Ishimori's procedure was first reexamined. Thallium was reduced with hydroxylamine hydrochloride, and potassium cyanide and ammonium citrate were added. The pH of the solution was adjusted to about 10 by adding ammonium hydroxide. The dithizone extraction was then carried out. In the absence of foreign metals, the recoveries were satisfactory as shown by the results marked by ** in Table III. However, when the procedure was applied in the presence of iron(III), the recoveries of thallium became extremely low and yet the blank became higher. The present investigation has confirmed that the method of Sill and Peterson[13] eliminated this difficulty.

Results obtained in applying the proposed method are collected in Table III. Most of the metals added were in the form of chloride, but some were sulfates or nitrates. It is seen that double nitric acid extraction is preferable to single extraction. In the presence of relatively large amounts of the metals reacting with dithizone, the extraction will have to be carried out more than three times. The recoveries of thallium were slightly low and it is believed that the application of a correction factor of +10% is advisable. If the values in the table are increased by this amount, the recoveries become generally within 5% of the theoretical values.

Summary

Procedure is given for the spectrophotometric determination of 1–10μg. of thallium with rhodamine B. Ammonium persulfate was also found to be as effective as bromine in oxidizing thallium preparatory to rhodamine B—benzene extraction. For the separation of thallium from other elements, univalent thallium is extracted with dithizone in chloroform from a basic solution containing cyanide and then transferred to an aqueous solution by shaking the chloroform with dilute nitric acid. The procedure provides for the presence of antimony, gallium, gold, iron and tungsten.

Government Industrial Research Institute, Nagoya, Kita-ku Nagoya

13) C. W. Sill and H. E. Peterson, *Anal. Chem.*, **21**, 1268 (1949).

Relation between Foaming Properties and the Structure of Surface Active Substances. I. Foaming Properties of Aqueous Soap and Sodium Dodecyl Sulfate

By Maresuke KASHIWAGI

(Received January 25, 1957)

Introduction

As was previously reported[1], the foaming power of aqueous sodium dodecyl sulfate (hereafter called SDS) is a function of concentration, and the critical micelle concentration (hereafter called cmc.) can be determined by this method. In a similar fashion, any other surface active substances may be closely correlated to the structure of its solution.

According to the foaming power measurement by Ross-Miles' method, the foaming power of SDS increases with concentration up to cmc. and above the cmc. it becomes nearly constant. In the light of this knowledge, the foaming power measurement of soap, a most typical surface active substance, carbon numbers of which range from ten to sixteen, was undertaken. The mechanism of foaming may be explained partly by Debye's theory[2] and at the same time by surface tension.

Since some inorganic ions are known to lower surface tension, the foaming properties of soap may be expected to be increased by the addition of those ions. In fact, the foaming power increases in the order of lyotropic series.

Experimental

Apparatus — The apparatus used is the same as that of Ross-Miles[3]. The schematic diagram and the dimension were described in the author's previous report[1]. For surface tension measurement DuNouy's tensiometer was used.

Materials — The analysis of SDS was described in the previous report[1]. Soap used here is sodium salt of fatty acids which were prepared using fatty acids purchased from Merck and purified. The analysis is shown in Table I.

Inorganic salts, (LiCl, NaCl, KCl and RbCl) were all given by the courtesy of Dr. Y. Murakami, Faculty of Science, University of Tokyo.

Measurement — The temperature is kept by the thermostat at 40 ± 0.1°C. All solutions are prepared under the same condition and the measurements are done right after the preparation of the solution, since soaps are very sensitive to temperature and time.

TABLE I
ANALYSIS OF FATTY ACIDS

Acid	M. P.		N. V.*	
	found	literature	found	theoretical
Capric	32.3	31.6	320.3	325.70
Lauric	45.1	44.2	278.0	280.09
Myristic	54.0	54.4	242.9	245.67
Palmitic	60.8	63.1	213.7	218.80

* N. V.....Neutralisation Value

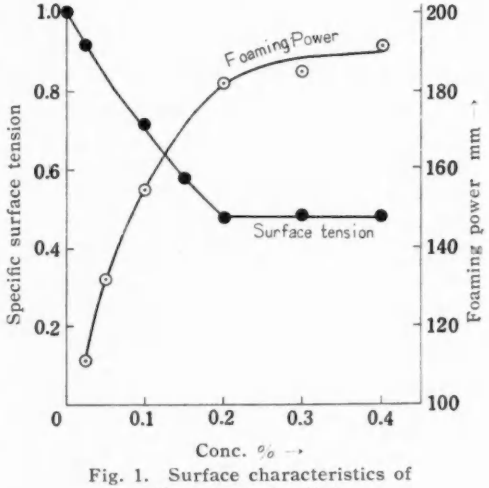

Fig. 1. Surface characteristics of sodium dodecyl sulfate.

Results

Fig. 1 shows foaming power (i. e. height of the foam part, expressed in mm) and specific surface tension against concentration of SDS. Specific surface tensions are calculated from values measured by DuNouy's tensiometer. By comparing these curves it can be seen that there is a correlation between foaming power and surface tension; that is, as foaming power

1) M. Kashiwagi, This Bulletin, **29**, 193 (1957).
2) P. Debye, *Ann. N. Y. Acad. Sci.*, **51**, 575-92 (1949).
3) J. Ross and G. D. Miles, *Oil and Soap.*, **18**, 99 (1941).

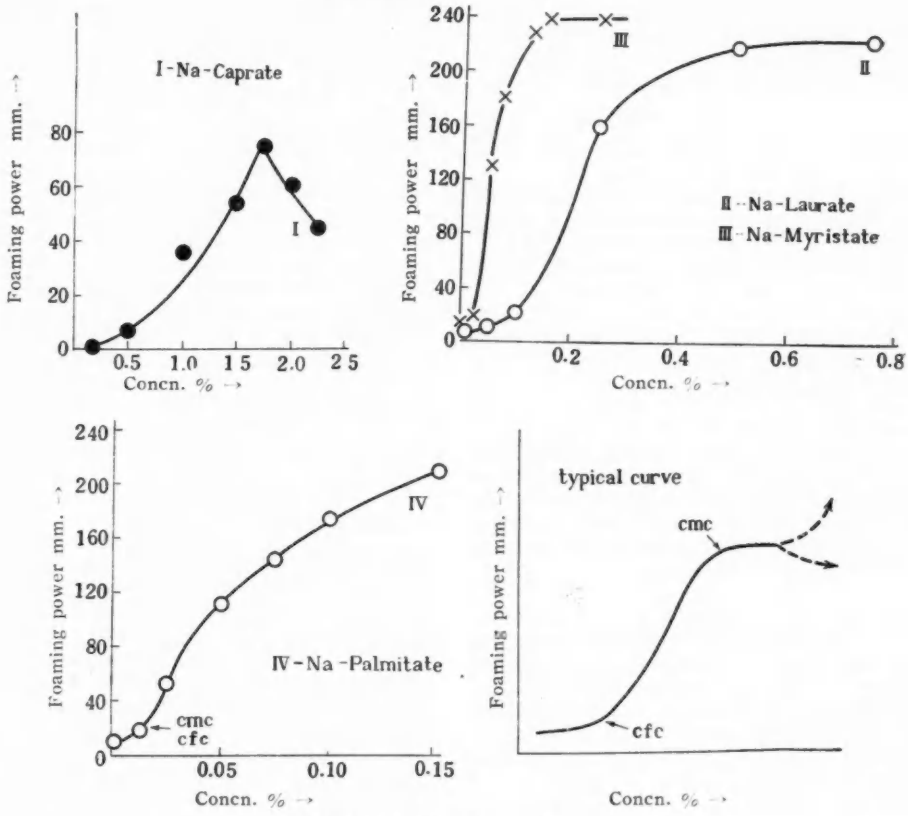

Fig. 2. Foaming power of soap.

increases, surface tension decreases and above the same cmc. both curves become practically constant.

Fig. 2 shows the foaming power of soap. As in the case of SDS already described, the tendency is again the same. The same sort of result was obtained for potassium soap by the other method; however, the method of Ross-Miles seems to be more accurate than this shaking method[4].

From the curves which appeared in Fig. 2, it was found that sodium myristate has more pronounced foaming power than others. Sodium stearate was also studied, but its foaming power was found to be too poor. Since the addition of inorganic ions is known to affect surface tension, it was thought to be interesting to add to soap neutral salts of the series lithium, sodium, potassium and rubidium chloride. Table II shows the influence of the addition of those inorganic salts on 0.1% sodium myristate.

TABLE II
INFLUENCE OF INORGANIC SALTS ON FOAMING POWER
(AVERAGE FOAMING POWER IN mm.)

Salt	Salt concn.	10^{-2} M	10^{-1} M
LiCl		244	salting out
NaCl		240	245
KCl		228	230
RbCl		228	220
None		210	210

It is demonstrated that inorganic ions raise the foaming power of soap in the order $Li^+ > Na^+ > K^+ > Rb^+$.

Nevertheless, the difference between each ion at the concentration of 10^{-2} M is only slightly noticeable and ten times increase in concentration of salt did not raise the foaming power noticeably.

4) M. Nakagaki and K. Shinoda, This Bulletin, **27** 367 (1954).

Discussion

Hobbs[5] derived the following expression by thermodynamic consideration of micelle formation from single molecule.

$$\log \text{cmc.} = -K_0\beta + \text{constant} \quad (1)$$

Where β is the number of carbon atoms in the chain and K_0 is constant.

Empirical values of cmc. determined by the foaming power measurement as appeared in Fig. 2 are shown, together with some constants from the measurement, in Table III.

Those measured values of cmc. were found to fit the above equation and the constants are calculated as follows,

$$\log \text{cmc.} = -0.314\,\beta + 1.796 \quad (2)$$

It might also be added that they are in good agreement with values determined by other methods[6].

Sodium palmitate deviates a little from the above equation, but this should be attributed to the fact that its cmc. can not be distinguished from cfc.

TABLE III

SOME PHYSICAL CONSTANTS OF SOAP

No. of carbon atoms	cmc. mol/l.	Critical* foam conc. M	Approximate expansion ratio at cmc.**
10	0.0902	0.05	19
12	0.0228	0.009	58
14	0.0049	0.001	58
16	0.0009	0.0009	28

* Critical foam concentration is defined by the author as the concentration at which foaming begins and below which foaming is negligibly small.

** Expansion ratio: V_f/V_l where V_f is the volume of foam converted from liquid state and V_l is the volume of liquid which has been converted into foam.

Although quantitative treatment has not yet been made, decrease in surface tension always seems to result in increase of foaming power as shown in Fig. 1.

For soap the same relationship seems to exist. Comparison of Fig. 2 with surface tension data of Powney and Addison[7] corresponds to this rule.

For foaming properties, the influence of ion seems to be more predominant than that of micelle, since foaming increases with concentration up to cmc. and above it becomes nearly constant. Debye[2] demonstrated through light scattering in soap solutions that, as the number of long chain ions per micelle is of the order of 100, single ionswill predominate below cmc. and above it their concentration will change only slightly. The effect of inorganic ions is in the order of lyotropic series as shown in Table II, but is only slightly noticeable. It is known that cmc. of some surfactants shifts on the addition of inorganic salts; however, change in cmc. is independent of the kind of salt, and depends only on the concentration of cation[8].

Summary

1) The foaming power measurement by Ross-Miles method was found to be useful for the study of surface active substances.

2) A general rule for the foaming power would be that it increases with concentration up to cmc., and above it, becomes nearly constant or somewhat decreases. The foaming power is also inversely proportional to the surface tension.

3) The cmc. and other physical constants can be determined by the foaming power measurement.

4) Ion rather than micelle is presumed to be predominant with respect to foaming properties.

5) Effect of inorganic ions on foaming is slightly in the order of lyotropic series, namely $Li^+ > Na^+ > K^+ > Rb^+$, just before salting out.

The author expresses deep appreciation to Mr. H. Ezaki for permitting the publication and Dr. Y. Murakami for supplying inorganic salts.

Mitsuwa Chemical Laboratory
Sumidaku, Tokyo

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6) E. K. Goette, *J. Colloid Sci.*, **4**, 459 (1949).
7) J. Powney and C. C. Addison, *Trans. Faraday Soc.*, **34**, 372 (1938).
8) M. L. Corrin and W. P. Harkins, *J. Am. Chem. Soc.*, **69**, 682 (1941).

Syntheses of 3-Alkyl-naphtho(1.2-b)furan-2-carboxylic Acids

By Yuriko TANAKA

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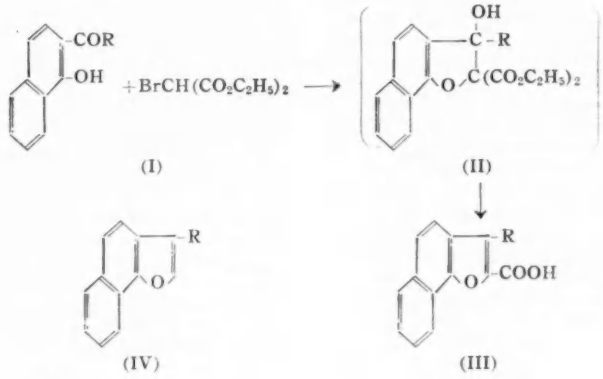
In connection with other synthetical works three 3-alkyl-naphtho(1.2-b)furan-2-carboxylic acids (III R=CH_3, C_2H_5, *n*-C_3H_7) were synthesized.

Search of literature revealed that of these three compounds only 3-methyl-naphtho(1.2-b)furan-2-carboxylic acid had been reported[1], but those synthetical methods are not preferable because of the complexity and the poor yield. Tanaka[2] reported a new general synthetic method for coumarones (benzofurans), and by using this method he synthesized phenanthro(1.2-b)furan derivatives[3]. For the syntheses of the substances mentioned above, his method was applied.

2-Aceto-1-naphthol (I, R=CH_3) and ethyl bromomalonate when refluxed in acetone in the presence of anhydrous potassium carbonate gave an oily substance, the structure of which is assumed to be II (R=CH_3). The last, without further purification, was hydrolysed with alcoholic potash and the carboxylic acid III(R=CH_3) was obtained. An attempt to decarboxylate the acid (III, R=CH_3) to 3-methyl-naphtho(1.2-b)furan (IV, R=CH_3) by refluxing in quinoline with copper powder[2] ended fruitless; by this procedure an oily substance with a peculiar smell of coumarones was obtained, but neither this oil nor its picrate showed satisfactory analytical value. As for the picrate, its analytical disagreement is likely due to its instability.

Starting from 2-propionyl- (I, R=C_2H_5) and 2-butyryl-1-naphthol (I, R=*n*-C_3H_7), the corresponding naphtho(1.2-b)furan-2-carboxylic acid (III, R=C_2H_5 and R=*n*-C_3H_7) were likewise synthesized in rather good yield (about 40%). Attempts to obtain the compounds IV (R=C_2H_5; C_3H_7) through decarboxylation of the corresponding acids III (R=C_2H_5; C_3H_7) were again unsuccessful just like the case III (R=CH_3) already mentioned.

The synthetic method used in the present paper is far superior to those described in the old literatures[1,*], so far as naphthofuran-2-carboxylic acids are concerned. The facts that the last acids hardly ever undergo decarboxylation are already stated in the literature[1c]. On the other hand benzofuran-2-carboxylic acids are smoothly[2] and phenanthro(1.2-b)furan-2-carboxylic acids are with difficulty decarboxylated[3]. Since the different behavior of decarboxylation of these



1) (a) A. Hantzsch, *Ber.*, **19**, 1303 (1886). (b) R. Stoermer, *Ann.*, **312**, 313 (1900). (c) St. v. Kostanecki and J. Tambor, *Ber.*, **42**, 908 (1909).

2) S. Tanaka, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **72**, 307 (1951); ibid., **73**, 282 (1952); *J. Am. Chem. Soc.*, **73**, 872 (1951).

3) S. Tanaka and S. Kawai, Unpublished work.

* Naphtho(2.3-b)furan derivatives were synthesized by Stoermer (see ref. (1b)) and K. Takeda, T. Schimada and K. Kitanouchi, *J. Pharm. Soc. Japan*, **70**, 268 (1950).

polynuclear benzofuran-2-carboxylic acids attracted the author's interest, the present writer wishes to re-examine the decarboxylation of other sorts of 3-alkyl-naphtho-(1.2-b)furan-2-carboxylic acid in the future.

Experimental[4]

3-Methyl-naphtho(1.2-b)furan-2-carboxylic Acid (III, R=CH_3) 2-Aceto-1-naphthol (8 g.), ethyl bromomalonate (10.4 g.), freshly dehydrated potassium carbonate (8 g.) and anhydrous acetone (50 ml.) were mixed together and the whole was gently refluxed in a water bath for ten hr. After distilling off the main part of the solvent, the residue was mixed with water and acidified with dilute mineral acid and then extracted with ether. The ethereal extract was washed with water, dried and the ether was removed, giving a dark brown oily substance. Without purification it was dissolved in alcoholic potash (alcohol 80 ml., potassium hydroxide 8 g., water 4 ml.), and then refluxed on a steam bath for one hr. After removal of the solvent, the residue was dissolved in water, washed with ether, and acidified with mineral acid, yielding grayish white precipitates; yield, about 4 g. (41 %). Recrystallization from glacial acetic acid (with charcoal) gave III (R=CH_3) as faint yellow pillars of m.p. 255–256° (dec.)[5]. Its analysis does not show satisfctory coincidence with the theoretical ones, just as in the cases of many sorts of coumarone-2-carboxylic acids[2].

Anal. Found: C, 73.21; H, 4.56. Calcd. for $C_{14}H_{10}O_3$: C, 74.33; H, 4.46 %.

Ethyl 3-Methyl-naphtho(1.2-b)furan-2-carboxylate The above-mentioned carboxylic acid (1 g.) was dissolved in absolute alcohol (10 ml.) containing 5 % of hydrogen chloride gas and the whole was refluxed in a water bath for five hr. After removal of the solvent, the residue was dissolved in ether, washed successively with aqueous sodium carbonate and water, dried and the ether was removed, leaving crystals (0.5 g.). The crude crystals were recrystallized from alcohol, giving ethyl ester as colorless flat columns of m.p. 107–108°[6].

Anal. Found: C, 75.10; H, 5.50. Calcd. for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55 %.

3-Ethyl-naphtho(1.2-b)furan-2-carboxylic Acid (III, R=C_2H_5) 2-Propionyl-1-naphthol (4.3 g.), ethyl bromomalonate (5 g.), potassium carbonate (3.1 g.) and acetone (60 ml.) were mixed together and the whole was refluxed in a water bath for ten hr. under exclusion of moisture. A similar treatment of the case with methyl derivative gave 2.2 g. (43 %) of crude crystals of carboxylic acid. Recrystallization from benzene gave III (R=C_2H_5) as colorless scales of m.p. 218–219°.

Anal. Found: C, 75.04; H, 4.94. Calcd. for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03 %.

3-*n*-Propyl-naphtho(1.2-b)furan-2-carboxylic Acid(III, R=*n*-C_3H_7) 2-Butyryl-1-naphthol (6 g.), ethyl bromomalonate (7.5 g.), potassium carbonate (5 g.) and acetone (65 ml.) were mixed together and the whole was refluxed in a water bath for ten hr. The same treatment as in the case with methyl derivative gave 3 g. (42 %) of the carboxylic acid. Recrystallization from chloroform (with charcoal) gave III (R=*n*-C_3H_7) as colorless needles of m.p. 203–204°.

Anal. Found: C, 75.35; H, 5.45. Calcd. for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55 %.

Attempted Decarboxylation of III— i) 3-Methyl-naphtho(1.2-b)furan-2-carboxylic acid (III, R=CH_3) (1 g.) and copper powder (0.1 g.) were refluxed in quinoline (10 ml.) on a wire gauze for 30 min. After cooling, ether (200 ml.) was added and the mixture was filtered from the copper. The ethereal solution was washed successively several times with 2-N-hydrochloric acid, water, aqueous sodium bicarbonate and then with water to remove quinoline and dried. This ethereal extract, when freed from the solvent, gave an oily substance. Distillation in vacuo gave an oil (0.5 g.), b.p. 66–70°/1 mm. A part of the oil solidified[7] on standing, and it has the characteristic smell of coumarones. There is a great difference between the analytical and the theoretical value.

The above-obtained semi crystals (0.2 g.) were dissolved in benzene (5 ml.) and to the solution was added picric acid (0.2 g.). The mixture was gently warmed on a steam bath for about 30 min. After cooling, yellow lustrous pillars were yielded, which showed m.p. 61–62° (dec.). Since the picrate thus obtained decomposed gradually in the recrystallization process, attempts to separate the picrate in pure state were unsuccessful.

ii) 3-Ethyl-, and 3-*n*-propyl-naphtho(1.2-b)-furan-2-carboxylic acids behaved analogously, their decarboxylation being difficult.

This research was supported by a Grant-in-Aid from the Ministry of Education.

Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Setagaya-ku Tokyo

4) All melting points were un-corrected.
5) See ref. (1a). Hantzsch gave m. p. 243-245° (dec.).
6) See ref. (1a). Hantzcsh gave m. p. 108°.
7) See ref. (1c). Kostanecki and Tambor gave m. p. 38°, b. p. 302-304°/720 mm.

Coprecipitation of a Trace Amount of Cesium with Thallous Salts

By Noboru YAMAGATA, Toshiko YAMAGATA and Sadakata WATANABE

(Received November 15, 1956)

Introduction

Direct separation of carrier-free radioactive cesium-137 from other fission activities has usually been accomplished, in the first step, by the use of the ammonium or the potassium ion as carrier[1]. The second step, the separation of cecium from the carrier ions is, however, fairly difficult, especially from potassium.

Coprecipitation of a trace amount of cesium with a thallous salt can be employed for this purpose, followed by oxidation to thallic state and precipitation as hydroxide.

The following experiments deal with the coprecipitation of a trace amount of cesium with thallous (1) dipicrylaminate, (2) cobaltinitrite, (3) chloroplatinate, (4) phosphotungstate, (5) silicotungstate, (6) phosphomolybdate, (7) copper ferrocyanide, (8) chloride, (9) bromide, (10) iodide and (11) sulfide.

The other well known precipitation methods, such as iodobismuthate, perchlorate and periodate method, were not tested, because these reagents oxidize thallous ions to thallic.

Experimental

The conditions of precipitation and filteration were chosen, from the viewpoint of practical convenience, to facilitate rapid precipitation and immediate filtration.

Unless otherwise specified in the following, the precipitating agent is added to the carrier-free cesium solution (^{137}Cs imported from U. S. A. in 1954, Batch No. 14) and then the thallous nitrate solution with constant agitation. The precipitate is filtered off or centrifuged after thirty minutes' agitation and another thirty minutes' digestion without stirring.

The activity was measured by the use of a Geiger-Müller tube of the mica end-window type and a Tracerlab's "1000"-scaler.

1. Dipicrylaminate Method[2]. — A proper quantity of carrier-free cesium solution (about 10^4 cpm. in 0.3 N hydrochloric acid) is taken in a 50 cc. Erlenmeyer flask and neutralized to thymol blue with 0.1 N sodium hydroxide solution. About 100% excess of 3% magnesium dipicrylaminate solution is added and the mixture is made up to 30 cc. After cooling for about half an hour in ice water, 1 cc. of 0.1 N thallous nitrate solution (containing about 20 mg. thallium) is dripped with constant stirring. The product is stirred for thirty minutes and set aside for another thirty minutes in ice water. The precipitate is filtered off and washed first with 2 cc. of ice water, then with two 2 cc. portions of diethyl ether at 0°C.

The filtrate and the washings are united, made up to 50 cc. with water and 5 cc. portions are evaporated up in small dishes, for their activity (A) to be measured. To the same volume of the solution, one tenth quantity of the radioactive cesium first taken is added and the activity (A') is measured after evaporation. The activity of cesium removed by coprecipitation (%) is represented as $100(A'-2A)/(A'-A)$.

2. Cobaltinitrite Method[3].—To the carrier-free cesium solution in a flask, the reagent (about 8 cc.), prepared from cobaltous nitrate and sodium nitrite, is added and diluted to 30 cc. Thallous nitrate solution is added dropwise with stirring, at room temperature. The precipitate is filtered off and washed twice with 10% acetic acid solution.

3. Chloroplatinate Method[4].—To the carrier-free cesium solution in a flask, about 50% excess of 5% aqueous chloroplatinic acid solution is added and diluted to 30 cc. The thallous nitrate solution is added dropwise with mechanical stirring, at room temperature. The precipitate is filtered off with a glass filter and washed twice with 98% ethyl alcohol. The solubility of thallous chloroplatinate in water is very small and an anhydrous condition as in the case of potassium determination is not necessary. The precipitate is usually colloidal and filtered with difficulty. With vigorous stirring, however, it becomes crystalline and is easily filtered.

4. Phosphotungstate Method.—To the carrier-free cesium solution in a flask, 2 cc. of 0.1 M solution of the reagent is added and diluted to 30 cc. with 3 N or 6 N hydrochloric acid. At 0°C or 60°C, with stirring, the thallous nitrate solution is added dropwise. The resulting precipitate

1) T. Shiokawa and M. Yagi, *Japan Analyst*, **5**, 220 (1956.)

2) R. B. Hahn and R. O. Backer, AECU-2903 (1955); E. B. Sandell, "Colorimetric Determination of Traces of Metals" London, (1950) p. 501.

3) R. Overstreet and L. Jacobson, Paper 286 of "Radiochemical Studies: The Fission Products." editted by H. B. Evans, Book 3, New York (1951); F. P. Treadwell and W. T. Hall, "Analytical Chemistry" Vol. 2, 8th ed. John Wiley and Sons, Inc., London (1931) p. 68.

4) "Gmelins Handbuch der Anorganischen Chemie" System Nr. 38, Verlag Chemie, Berlin (1940) p. 161.

is of colloidal nature and must be separated by centrifuging.

5. Silicotungstate Method[5].—The procedure is similar to that for the phosphotungstate method; 0.1 M solution of silicotungstic acid was used.

6. Phosphomolybdate Method[5].—To the carrier-free cesium solution in a flask are added 18 cc. of 0.15 N nitric acid, 0.15 g. of ammonium molybdate, and 0.3 cc. of conc. phosphoric acid, to be diluted to 30 cc. The thallous nitrate solution is added dropwise with stirring at 40–50°C, for the precipitate to be collected by centrifuging.

7. Copper Ferrocyanide Method[6].—To the carrier-free cesium solution in a flask are added 18 cc. of 0.15 N nitric acid, 5 cc. of 1/15M potassium ferrocyanide solution and the thallous nitrate solution. The resulting solution is cooled to 0°C. Five cc. of 1/20 M copper sulfate solution is added with constant stirring, at 0°C. The precipitate is collected by centrifuge. This method, originally described by H. L. Krieger et at.[6] did not use a thallium carrier.

8. Thallous Chloride Method.—To the carrier-free cesium solution, 3 N hydrochloric acid and distilled water are added to produce 30 cc. of 1 N acid solution. After being cooled to 0°C with constant stirring, this solution is treated with the thallous nitrate solution. The precipitate is filtered off and washed with 1 N hydrochloric acid at 0°C.

9. Thallous Bromide Method.—The cesium solution is submitted to a procedure similar to that mentioned above, by the use of hydrobromic acid.

10. Thallous Iodide Method[7].—Free iodine, occasionally found in hydroiodic acid, may oxidize thallous ion to thallic, interfering with the formation of thallous iodide. Potassium iodide was used instead of hydroiodic acid. To the carrier-free cesium solution in a flask, 1 cc. of glacial acetic acid and 5 cc. of 10% potassium iodide solution are added and diluted to 30 cc. The thallous nitrate solution is added with stirring, at 0°C or at room temperature. The precipitate is filtered off and washed first with 1% solution of potassium iodide in 1% acetic acid and then with acetone.

11. Thallous Sulfide Method.—The carrier-free cesium solution is evaporated up in a flask to eliminate the free hydrochloric acid and treated with the thallous nitrate solution and 5 cc. of 1 N acetic acid. The product is mixed well and neutralized with concentrated ammonia water with further addition of 1 cc. excess. The resulting solution is made up to 30 cc. and, after being heated to 60°C, bubbled with hydrogen sulfide for thirty minutes or for four hours. The precipitate is immediately filtered off and washed with ammoniacal ammonium sulfide solution.

5) L. E. Glendenin and C. M. Nelson, Paper 283 of "Radiochemical Studies: The Fission Products" ed. by H. B. Evans, Book 3, New York (1951); E. K. Hyde, *J. Am. Chem. Soc.*, **74**, 4181 (1952).

6) H. L. Krieger, B. Kahn and C. P. Straub, ORNL-1966 (1955).

7) "Gmelins Handbuch der Anorganischen Chemie" Syst. Nr. 38, Verlag Chemie, Berlin (1940) p. 160.

Results and Discussion

The group of methods shown in Table I represents successful coprecipitation; tracer amounts of cesium can be collected almost perfectly by these methods. From the view-point of avoiding contamination with cesium and rubidium which can be introduced from the used reagents containing alkali elements, the cobaltinitrite and the copper ferrocyanide method are not satisfactory. Chloroplatinic acid is rather expensive and is not suitable for practical use. Thus, dipicrylaminate or the phosphotungstate method is recommended, the former being considered to be more suitable. Dipicrylamine is very easily purified from metallic contaminants before use and the thallous salt of dipicrylamine containing cesium activity can be decomposed with a dilute mineral acid to precipitate free dipicrylamine, which is removed by extraction with an organic solvent. The extracted dipicrylamine can be recovered for further use.

The following cautions are, of course, needed for the practical use of this reagent:

1) As the precipitation of thallous dipircylaminate takes place in a slightly alkaline condition, iron, aluminum and other heavy metals must be previously removed.

2) Potassium, ammonium and rubidium ions form a precipitate with dipicrylamine; they must be absent in the solution.

In Table II, the results of unsuccessful coprecipitation are shown. Silicotungstic acid is an effective reagent for coprecipitation of a trace amount of cesium or francium[8], when the cesium ion is used as carrier, but, when the thallous ion is used, it failed to act as a trace-catcher.

Phosphomolybdic acid, which was recommended by H. L. Krieger et al.[6] as an efficient precipitant for cesium, also failed to be so when the thallous ion was used. In those cases, the failure of coprecipitation was supposed to be derived from the difference in crystal structure between cesium and thallous silicotungstate (or phosphomolybdate).

The examination of the separation of cesium activity from thallium and other fission activities is beyond the scope of this article. If any presumption could be possible, however, the results of the methods described in Table II should provide an important suggestion concerning the procedure for separation of thallium

8) E. K. Hyde, *J. Am. Chem. Soc.*, **74**, 4181 (1952).

TABLE I

COPRECIPITATION OF A TRACE AMOUNT OF CESIUM WITH THALLOUS SALTS (1)

Carrier Tl(I) mg.	Activity of carrier-free Cs, added cpm	Activity of Cs, co-precipitated cpm	Activity of Cs, collected %	Chemical yield of precipitation %	Temp. °C	Remarks
	(1) Dipicrylaminate method					
20.0	1620	1480	91.4	92.0	0	
20.0	1544	1379	89.3	91.0	0	
40.0	1645	1269	77.1	72.3	18	
40.0	1571	1174	74.7	71.8	18	
	(2) Cobaltinitrite method					
20.0	826	768	93.0	—	19	
40.0	1158	1126	97.2	—	19	
	(3) Chloroplatinate method					
20.0	1530	1387	90.7	98.9	19	
20.0	1615	1449	95.7	—	19	
	(4) Phosphotungstate method					
20.0	1926	1889	98.1	—	60	3 N
20.0	2041	1983	97.2	—	60	6 N
40.0	1950	1940	99.5	—	0	3 N
40.0	2210	2161	97.8	—	0	6 N
	(7) Copper ferrocyanide method					
0	2891	2870	99.3	—	0	
20.0	1449	1433	98.9	—	0	
40.0	1498	1484	99.1	—	0	

TABLE II

COPRECIPITATION OF A TRACE AMOUNT OF CESIUM WITH THALLOUS SALTS (2)

Carrier Tl(I) mg.	Activity of carrier-free Cs, added cpm	Activity of Cs, co-precipitated cpm	Activity of Cs, collected %	Chemical yield of precipitation %	Temp. °C	Remarks
	(5) Silicotungstate method					
*13.3	1620	1388	85.7	—	0	*Cs-
*13.3	1716	1466	85.4	—	0	carrier
20.0	1655	31	1.9	—	0	3 N
20.0	1603	23	1.4	—	0	6 N
	(6) Phosphomolybdate method					
20.0	1422	181	12.7	—	40-50	
40.0	959	57	5.9	—	40-50	
	(8) Chloride method					
40.0	1700	160	9.4	89.9	0	
60.0	1491	23	1.6	—	0	
	(9) Bromide method					
20.0	1457	34	2.4	96.5	0	
40.0	1658	229	14.1	98.0	0	
	(10) Iodide method					
20.0	1898	337	12.5	99.0	18	
20.0	1745	144	8.4	98.5	0	
	(11) Sulfide method					
20.0	1610	250	15.5	—	60	30 min.
20.0	1748	33	1.9	—	60	4 hr.

from a trace amount of cesium. Without being oxidized to the thallic state, the thallous ion can be separated from cesium by precipitation as halide or sulfide with a slight loss in cesium activity. The authors also tested the separation of thallium as thallic hydroxide after oxidation with bromine water. The result also proved promising.

Summary

The possibility of coprecipitation of a trace amount of cesium with various thallous salts has been studied. The following salts were proved to be efficient: dipicrylaminate, cobaltinitrite, chloroplatinate, phosphotungstate and copper ferrocyanide; of those the dipicrylaminate method was recommended.

Only partial coprecipitation of cesium took place with thallous silicotungstate, phosphomolybdate, chloride, bromide, iodide and sulfide.

Kiriu College of Technology
Gunma University, Kiriu

Carrier-free Separation of Cesium from Fission Products by the Use of Coprecipitation with Thallium(I) Dipicrylaminate

By Noboru YAMAGATA and Sadakata WATANABE

(Received January 12, 1957)

The authors showed in the previous report[1] an efficient coprecipitation of a trace amount of cesium with thallium (I) dipicrylaminate and suggested several possible ways of its separation from the carrier. The present report deals with its separation from both the carrier ion and other fission activities, including ^{90}Sr–^{90}Y, ^{106}Ru–^{106}Rh, ^{95}Zr–^{95}Nb and rare earth elements.

Coprecipitation of Other Fission Activities with Thallium(I) Dipicrylaminate

The radionuclides which coprecipitate with thallium(I) dipicrylaminate were clarified in order to find the later process of separation.

The radionuclides in question were separated from mixed fission products, about one year old, by ion-exchange method[2] and each fraction was converted into nitric acid solution. Their suitable quantities were submitted to direct precipitation with thallium(I) dipicrylaminate after neutralization with sodium hydroxide.

The following percentages of applied activities were found in the directly precipitated thallium(I) dipicrylaminate.

Rare earth elements	0.20
^{95}Zr–^{95}Nb	0.73
^{90}Sr–^{90}Y	0.53
^{106}Ru–^{106}Rh	0.38
U	56.8[3]

Those figures indicate that some scavenging pretreament is necessary in the practical separation of cesium from mixed fission products.

Separation of Cesium Activity from Thallium(I) Dipicrylaminate

For the separation of cesium activity from thallium(I) carrier, three processes were tested: (1) precipitation, (2) ion-exchange and (3) extraction.

(1) Precipitation. Hydrous ferric oxide carries down various kinds of fission activity, but a negligible amount of cesium. Since the thallium(III) ion was expected to behave similarly, the coprecipitation of fission activities with thallium(III) hydroxide was tested.

An acid solution containing 0.1 m mol. of the thallium(I) ion was mixed with a proper quantity of fission products, oxidized with chlorine water, and neutralized to about pH 9. Immediate filtration

1) N. Yamagata, T. Yamagata and S. Watanabe, This Bulletin, **30**, 577 (1957).
2) K. Kimura et al., *Japan Analyst*, **3**, 335 (1954).
3) The value for uranium is so high that, when it is present in fission products, it must be previously removed by solvent extraction.

resulted in about 83.6–85.8% coprecipitation of overall activities. The loss of a trace amount of cesium under the same condition was only 0.3–0.4% and about 2% of thallium entered the filtrate; the latter could be removed, however, by extraction or ion-exchange method as described later.

In practice, the starting material is thallium(I) dipicrylaminate containing a trace amount of cesium; the precipitate is dissolved in hot water and acidified with hydrochloric acid. The precipitate of free dipicrylamine can be easily removed by filtration without loss in cesium activity.

(2) Ion-exchange. Since, the selectivity coefficients of Dowex 50 given by W. C. Bauman and J. Eichhorn[4] are 2.04 for K_H^{Cs} and 8.60 for $K_H^{Tl(I)}$, chromatographic separation of cesium from thallium(I) is expected to be easily accomplished, when both elements are present in appreciable amounts. The present investigation, however, concerns the separation of a trace amount of cesium from a large quantity of thallium.

The selectivity coefficients of the cation exchanger Dowex 50 X-12 for cesium and thallium(I) were determined by the batch method described by one of the authors[5]. The results, shown in Table I, indicate

TABLE I
SELECTIVITY COEFFICIENTS OF THALLIUM(I) AND CESIUM
(Dowex 50, X-12)

Selectivity coefficients		Molar fraction in solution α	Molar fraction in resin β
$K_H^{Tl(I)}$	18.5	0.0119	0.182
	19.8	0.0084	0.143
K_H^{Cs}	5.8	0.078	0.33
	10	0.0060	0.058
	12	5.8×10^{-4}	0.0069
	13	1.1×10^{-5}	1.4×10^{-7}

that the K_H^{Cs} value for an infinitely dilute solution is greater by twice or more, as compared with the ordinary value. The difficulty, which the simple chromatographic separation involves, was also confirmed by dynamic flow tests.

Another promising method of separation by the use of ion-exchange resin is the utilization of the strong adsorbability of thallium(III) ions upon an anion-exchange resin in hydrochloric acid solution[6]. Selectivity coefficients were determined for three kinds of anion-exchanger by the batch method. Dowex 1 was proved to be the best as shown in Table II, the

TABLE II
SELECTIVITY COEFFICIENTS OF THALLIUM(III) IN HYDROCHLORIC ACID SOLUTION

Concentration of HCl	Anion exchanger	Selectivity coefficient	Molar fraction in solution α	Molar fraction in solution β
1 N	Dowex 1 X-8	370	5.5×10^{-4}	0.170
	Dowex 2 X-10	250	8.1×10^{-4}	0.169
	Amberlite IRA-410	110	1.4×10^{-3}	0.134
4 N	Dowex 1 X-8	3400	9.8×10^{-5}	0.249
	Dowex 2 X-10	820	3.6×10^{-4}	0.226
	Amberlite IRA-410	360	5.9×10^{-4}	0.174

ion-exchange capacity being 2.72 meq. per gram of resin dried at 72°C. Dynamic flow experiments, by use of ^{204}Tl as an indicator for breakthrough, also proved this method to be satisfactory

3) Extraction. It is well known that the thallium(III) ion can be extracted from hydrochloric or hydrobromic acid medium with diethyl ether[7]. The authors also determined the efficiency of extraction for the removal of thallium from a trace amount of cesium.

Twenty ml. of the acid solution was shaken with the same volume of diethyl ether, saturated with hydrochloric or hydrobromic acid of corresponding concentration. In the case of 12 N hydrochloric acid and 6 N hydrobromic acid, the procedure was modified so that the acid solution, previously saturated with ether, was shaken with pure ether. When thallium(III) was shaken, several drops of saturated chlorine water were added to avoid possible reduction of thallium.

The results are shown in Table III. The extraction of thallium(III) and the recovery of the cesium activity were satisfactory, when the concentration of acid was kept 1 to 4 N. The results also

4) W. C. Bauman and J. Eichhorn, *J. Am. Chem. Soc.*, **69**, 2830 (1947).
5) N. Yamagata, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **87**, 513 (1957).
6) K. A. Kraus and F. Nelson, A/Conf. 8/P/837 (1955).
7) I. Wada and R. Ishii, *Bull. Inst. Phys. Chem. Research, Tokyo* **13**, 264 (1934).

TABLE III
EXTRACTION OF THALLIUM(III) AND OTHER ELEMENTS FROM HYDROCHLORIC AND HYDROBROMIC ACID SOLUTION WITH DIETHYL ETHER

Percentage of the element remaining in HCl solution after one extraction

	Concn. of HCl				
	1 N	2 N	4 N	6 N	12 N
Carrier-free Tl(III)	0.79	1.6	0.83	2.8	85
0.1 m mol. Tl(III)	0.69	1.6	0.64	3.2	83
Carrier-free Cs	98.6	99.8	98.2	99.4	99.2
Mixed F.P.	99.0	—	99.0	99.0	99.0
Tracer U(VI)	89.3	—	91.2	—	—

Percentage of the element remaining in HBr solution after one extraction

	Concn. of HBr			
	1 N	2 N	4 N	6 N
Carrier-free Tl(III)	2.5	0.59	1.3	77
0.1 m mol. Tl(III)	0.41	0.45	1.7	30

indicated that, when 0.1 m mol. of thallium (III) was extracted with ether only once, about 1% or 0.2 mg. of this element entered the cesium solution.

In the practical separation of cesium, the starting material is thallium(I) dipicrylaminate which is insoluble in diethyl ether. An organic solvent, which is immiscible with water and dissolves the precipitate, would be more useful than diethyl ether, because it also removes the free dipicrylamine.

For this purpose, methylisobutyl ketone was found to be the best. It readily dissolves both thallium(I) dipicrylaminate and free dipicrylamine. The extraction of thallium(III) with methylisobutyl ketone was studied from hydrochloric acid solution, and the results are shown in Table IV.

TABLE IV
EXTRACTION OF THALLIUM(III) AND OTHER ELEMENTS FROM HYDROCHLORIC ACID SOLUTION WITH METHYLISOBUTYL KETONE

Persentage of the element remaining in HCl solution after one extraction

	Concn. of HCl			
	1 N	2 N	4 N	6 N
0.1 m mol. Tl(III)	0.89	0.56	1.0	0.73
Carrier-free Cs	99.5	99.6	99.7	99.7
Tracer U(VI)	84.4	—	89.2	—

Proposed Procedure

Step 1. To the sample of fission material[8], add iron(III) and strontium nitrate solution equivalent to 20 mg. of iron and 5 mg. of strontium. Add sodium hydroxide solution of proper strength until the solution is basic to thymol blue (pH 8–9) and then 1 ml. of 1 M sodium carbonate solution. Filter and wash with a little water.

Step 2. After the neutralisation of the filtrate, if necessary, to pH 8–9, add about 100 % excess of sodium dipicrylaminate solution (3 % in water)[9] and cool the resulting solution for about half an hour in ice water. With constant stirring, add 1 ml. of 0.1 N thallium(I) nitrate solution dropwise, and continue the stirring for thirty minutes at 0°C. Filter the precipitate and wash first with 2 ml. of ice water, and then with two 2 ml. portions of diethyl ether at 0°C.

Step 3. Take up the precipitate in 5–10 ml. of methylisobutyl ketone into a separatory funnel. Add 1 ml. of saturated chlorine water and 5–10 ml. of 2 N hydrochloric acid. Shake vigorously for one minute and take the aqueous layer in another separatory funnel.

Step 4. To the separatory funnel, add the same volume of methylisobutyl ketone and shake for one minute vigorously. Evaporate the aqueous layer to dryness in a small counting dish and mount.

The results of recovery and separation tests are shown in Table V. The gross decontamination factor is greater than

TABLE V
RECOVERY AND SEPARATION TESTS

Activities taken		^{137}Cs activity found	Recovered Cs
	cpm	cpm	%
F.P.	1.1×10^5	1142	—
F.P.	1.1×10^5		
^{137}Cs	1149	2148	93.8
R.E.	1.5×10^5		
Sr-Y	1×10^4		
Ru-Rh	2×10^4	1002	87.2
Zr-Nb	2×10^3		
^{137}Cs	1149		

8) The sample must not contain potassium or rubidium, since they will be present in the final product as inert solids and removed with difficulty. If uranium is present in the starting sample, it must be removed previously.

9) E. B. Sandell, "Colorimetric Determination of Traces of Metals" Interscience Pub. Inc., New York (1950) p. 501.

10^4, although the proposed procedure is only valid for about one year old fission products; when cesium is to be prepared from or analyzed in a fresher sample, the procedure should be modified.

Summary

A procedure has been presented for the separation of carrier-free cesium from the fission products. The method makes use of coprecipitation with thallium(I) dipicrylaminate followed by solvent extraction with methylisobutyl ketone in the presence of hydrochloric acid and an oxidizing agent. The recovery of active cesium is about 90% and the gross decontamination factor is more than 10^4.

Kiriu College of Technology
Gunma University, Kiriu

Rapid Analysis of Gamma-Emitters Using Gamma-Ray Scintillation Spectrometer. I. Quantitative Analysis of ^{134}Cs—^{137}Cs *Mixture*

By Fumio AOKI*, Toshio KUROSAWA* and Seishi YAJIMA**

(Received January 25, 1957)

Introduction

Rapid determination of individual species in a mixture of radionuclides will be required in many cases, such as processing of fission products, activation analysis, and chemical, biological or metallurgical experiments with several kinds of radionuclide.

Since the advent of electronic scintillation counting techniques, the application of scintillation spectrometers has been introduced to the study of analysis. Several investigations[1] on the analysis of radionuclide mixtures were reported, and the quantity of each nuclide was obtained from the area under the photopeak resolved by the spectrometer.

The authors have been investigating the possibility of quantitative determination of two nuclides which cannot be resolved by the spectrometer. This report is the result of the study on ^{134}Cs—^{137}Cs mixture.

Quantitative Measurement of ^{134}Cs—^{137}Cs Mixture

Principal gamma-energies emitted from ^{134}Cs[2] are 0.57 MeV, 0.60 MeV and 0.79 MeV, others being negligible in intensity. The pulse height scan shows two photopeaks at 0.79 MeV and at 0.57 MeV and 0.60 MeV (unresolved).

The gamma-energy of ^{137}Cs is 0.66 MeV; the pulse height scan shows one photopeak at 0.66 MeV.

In the presence of both ^{134}Cs and ^{137}Cs, two peaks appear as shown in Fig. 1. Let A be the area under 0.6 MeV photopeak (0.57 MeV, 0.60 MeV and 0.66 MeV photopeaks being superposed), then,

$$A = A_4 + A_7$$

where A_4 and A_7 are the areas under the real photopeaks due to ^{134}Cs and ^{137}Cs near 0.6 MeV respectively. Or it is approximately obtained from the following expression,

$$A = \sum_a^b \gamma \times E$$

where

γ: counts per minute per channel width,
E: increment of energy equal to the channel width,
a and b: minimum points of the pulse height scan (Fig. 1).

So far as the geometry is fixed through out the measurement, and an identical apparatus is used, the pulse height scan normalized to the peak height of the principal gamma-energy is independent of the activity for a gamma-emitter[1]. Hence similar curves will be obtained by the

* Government Chemical Industrial Research Institute, Tokyo, Shibuya, Tokyo.
** Japan Atomic Energy Research Institute.

1) R. E. Connally and M. B. Leboeuf, *Anal. Chem.*, **25**, 1095 (1953); D. H. Peirson, *Atomics*, Sept. 316 (1956); U. L. Upson, R. E. Connally and M. B. Leboeuf, *Nucleonics*, **13**, No. 4, 38 (1955).
2) J. M. Hollander, I. Perlman and G. T. Seaborg, *Rev. Mod. Phys.*, **25**, 552 (1953).

spectrometer scans for the gamma-emitter, and A_4 is calculated as follows:

$$A_4 = \gamma_{max} \times C$$

where γ_{max} is the height of the 0.79 MeV photopeak, which is not affected by the ^{137}Cs pulse height distribution, and C is a constant; the value of the latter is obtained from careful measurements of ^{134}Cs standard.

A and γ_{max} (A_4) are obtained from the pulse height scan; hence A_7 is calculated. Through the comparison of γ_{max} (or A_4) and A_7 with those of a mixture of ^{134}Cs and ^{137}Cs of a known composition, their quantities will be found.

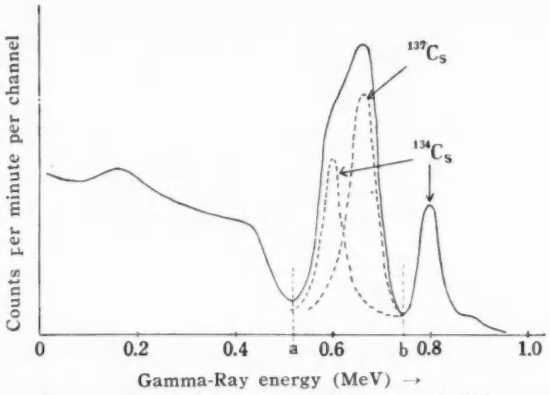


Fig. 1. Gamma-Ray spectrometer scan of ^{134}Cs—^{137}Cs mixture.

Experiment

The block diagram of the gamma-ray scintillation spectrometer (Atomic Instrument Co. Model 513) used in the experiment is shown in Fig. 2.

Before the quantitative measurement, the authors had ascertained the counting loss with ^{134}Cs and the results are shown in Fig. 3. The linearity of the counts vs. the quantity held up to 1×10^5 counts per minute in total counts and 5×10^3 counts per minute per channel width (0.02 MeV) in peak counts.

The chemical form of cesium was CsCl in aqueous solution. It was diluted to about 0.1 μC/ml with demineralized water. Mixed samples of ^{134}Cs—^{137}Cs were prepared as shown in Table I, taken in glass tubes of equal shape and size, and dried up. All residue remained on the bottom. Each glass tube has 15 mm outside diameter, which fits the geometry of the well of the NaI(Tl) crystal (see Fig. 2); it has 0.2g/cm^2 wall thickness. The absorption of the gamma-rays by the glass tube is undoubtedly negligible.

TABLE I
COMPOSITIONS OF SAMPLES

Nuclides	Quantities (ml)										
^{134}Cs	1	1	1	1	1	1	0	2	3	4	5
^{137}Cs	0	1	2	3	4	5	1	1	1	1	1

One ml. portion each of the ^{134}Cs and the ^{137}Cs were taken as arbitrary standards, which were carefully measured three times. The measuring system was switched on about three hours before the measurement for stabilization. Every sample was put into the well of the crystal, when its activity was measured.

The results obtained in 0.02 MeV channel width are shown in Table II and III. As their absolute activities were unknown, they were temporarily described by volume (ml.) of the solutions. The area under 0.6 MeV photopeak was calculated by summing up the counts from

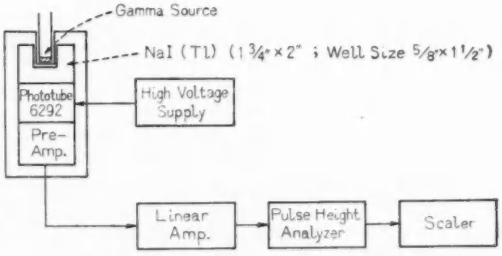


Fig. 2. Block diagram of scintillation spectrometer.

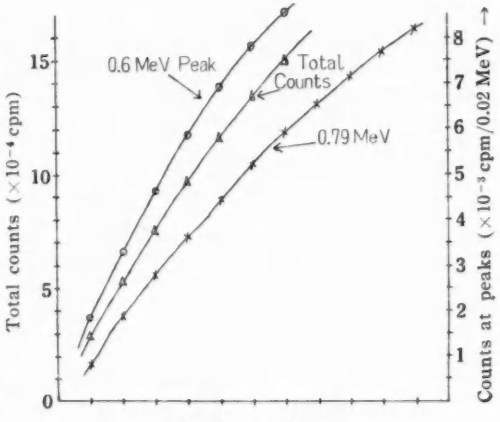


Fig. 3. Counting loss of the spectrometer.

a (0.51 MeV) to *b* (0.73 MeV) of Fig. 1, both of which were minimum points of the spectra.

Discussion

Concerning a mixture of ^{134}Cs and ^{137}Cs, the 0.79 MeV photopeak of ^{134}Cs is scarcely

TABLE II

ANALYSIS OF THE STANDARDS

Nuclides	Quantity (ml)	γmax (0.79 MeV) (cpm/V)	Area under 0.6 MeV peak (cpm)	$C\left(\frac{\text{Area}}{\text{max}}\right)$
^{134}Cs	1	572±3.2%	9.030±0.8%	17.13±3.3%
^{137}Cs	1	—	9.766±0.3%	—

TABLE III

ANALYSIS OF MIXTURES

Samples ^{134}Cs/^{137}Cs	γmax 0.79 MeV cpm/ 0.02 MeV	Area 0.6 MeV cpm	^{134}Cs			^{137}Cs		
			A_4 cpm	Quantity ml	Error %	A_7 cpm	Quantity ml	Error %
1/1	555	19,230	9,509	1.05	+ 5.3	9,721	0.99	− 0.5
1/2	532	23,126	9,080	1.00	+ 0.6	14,046	1.54	−28.0
1/3	537	32,388	9,165	1.01	+ 1.5	23,223	2.53	−20.7
1/4	633	44,182	10,804	1.19	+19.7	33,379	3.42	−14.5
1/5	505	48,841	8,619	0.95	− 4.5	40,222	4.14	−17.6
2/1	1,071	28,816	18,349	2.03	+ 1.6	10,467	1.07	+ 7.2
3/1	1,621	35,552	27,775	3.07	+ 2.5	7,777	0.79	−20.4
4/1	1,984	45,857	33,998	3.76	− 5.9	11,859	1.21	+21.4
5/1	2,694	56,713	46,160	5.11	+ 2.2	10,533	1.08	+ 8.1

affected by the ^{137}Cs pulse height distribution. It may be considered that this is the reason why the error for ^{134}Cs quantity is small and apt to come on the positive side. (see Table III).

Beta-rays emitted from ^{134}Cs (0.65 MeV: 75%, 0.09 MeV: 25%) and ^{137}Cs (0.51 MeV: 92%, 1.17 MeV: 8%)[2] are almost absorbed by the 0.2 g./cm^2 glass tube wall; about 80–90 % of beta-rays incident on the NaI (Tl) crystal are scattered out before being stopped[3]. Therefore the effect of beta rays would be negligible.

If a pulse height scan of a mixture of two nuclides shows two photopeaks and the high energy one involves two peaks of each nuclide, the quantitative determination will be a little more complicated.

The authors wish to thank Dr. Shogo Uchida, Director of the 1st Division, Mr. Kenichi Hashimoto and Dr. Toshio Nakai for encouraging the prosecution of the work.

Government Chemical, Industrial Research Institute, Shibuya
Tokyo

3) K. Siegbahn, "Beta- and Gamma-Ray Spectroscopy", North-Holland Publishing Co., Amsterdam (1955), p. 134.

*Determination of Critical Micelle Concentration of Detergent in Non-polar Solvent by Ultraviolet Absorption Spectra**

By Ayao KITAHARA

(Received February 6, 1957)

Micelle formation of detergents in non-polar solvents has been recently ascertained by many authors[1-4]. However, the existence of a concentration for micelle formation (CMC) in non-polar solvents is now questionable. Singleterry et al. have suggested the existence of the CMC of alkyl aryl carboxylate and sulfonate in benzene[3,5]. The present author has pointed out the existence of the apparent CMC in benzene solution of higher alkyl ammonium carboxylate by solubilization of water[6]. Pink et al. have not recognized the CMC in the case of a non-polar solution of a metal soap[4]. It seems, therefore, that the existence of the CMC in a nonpolar solvent is worth investigating by other methods and materials**.

In order to make a further study on the existence of the CMC in a non-polar solvent, the concentration dependence of the ultraviolet absorption spectrum in cyclohexane solution of detergent was studied in the present investigation. The result is compared with that of solubilization of water, and the existence of the CMC is discussed. The determination of the CMC by the change of the ultraviolet spectra was originally made by Harkins et al. with aqueous solution[7]. But the behavior of the change of the spectra are different from that of this paper.

Experimental

Material: Dodecyl ammonium benzoate and octadecyl ammonium benzoate were used as detergents. They were prepared by heating the mixture of higher amine with an equivalent amount of benzoic acid at about 70°C. Boiling points of dodecylamine and octadecylamine used here were 131-133°C/15 mm and 188-190°C/4 mm, respectively. Benzoic acid showed the melting point of 120-121°C. Dodecyl ammonium benzoate was used without further purification, because it was soluble in any solvent. Octadecyl ammonium benzoate was recrystallized from petroleum ether. Both were dried *in vacuo* over anhydrous calcium chloride. The melting point of the former was 40-42°C and that of the latter was 64.0-65.5°C. Cyclohexane was purified until it showed no absorption in the range longer than 230 mμ and then dried and redistilled.

Method: Ultraviolet absorption spectra were measured with Shimazu photoelectric spectrophotometer. In order to gain the absorbance of higher accuracy in the concentration range used here, all measurements were carried out with use of a quartz cell of a light path of 1.0 mm, which was obtained by means of the insertion of a quartz block of 9.0 mm thick into a 10.0 mm quartz cell. The absorption spectra of cyclohexane solutions of dodecyl ammonium benzoate and of octadecyl ammonium benzoate were observed in the range from 230 mμ to 300 mμ with varying concentration of detergent from 1×10^{-3} to 4×10^{-2} mole/l. The point-by-point absorbance measurements were carried out at intervals of 0.5 mμ at the neighborhood of the peak. Each solution was made by dilution of a prepared stock solution. Absorption measurement was carried out immediately after every dilution.

The limiting amount of water solubilized into cyclohexane solutions of dodecyl ammonium benzoate and of octadecyl ammonium benzoate was determined at various concentrations of detergent. The method of the measurement was similar to that of the previous paper[6]. The temperature was kept at 20 ± 2 and 30 ± 2°C in both measurements of spectrum and solubilization.

Results and Discussion

Existence of CMC: Absorption peaks appeared at 263, 270 and 276.5-277 mμ on the ultraviolet spectra of dodecyl ammonium benzoate and of octadecyl ammonium benzoate in cyclohexane. These absorption peaks are corresponding to the C-band of benzoic acid in cyclohexane, which has

* This paper was read at the Symposium on Colloid and Surface Chemistry held on November 18, 1956 at Tokyo University under the auspices of the Chemical Society of Japan.

1) L. Arkin and C. R. Singleterry, *J. Am. Chem. Soc.*, **70**, 3965 (1948).
2) M. van der Waarden, *J. Colloid Sci.*, **5**, 448 (1950).
3) S. Kaufman and C. R. Singleterry, *J. Colloid Sci.*, **7**, 453 (1952).
4) S. M. Nelson and R. C. Pink, *J. Chem. Soc.*, **1952**, 1744.
5) S. Kaufman and C. R. Singleterry, *J. Colloid Sci.*, **10**, 139 (1955).
6) A. Kitahara, This Bulletin, **28**, 234 (1955); **29**, 15 (1956).

** C. C. Addison and C. G. L. Furmidge have recently reported a CMC of alkylpyridinium iodides in xylene (*J. Chem. Soc.*, **1956**, 3229).

7) W. D. Harkins, H. Krizek and M. L. Corrin, *J. Colloid Sci.*, **6**, 576 (1951).

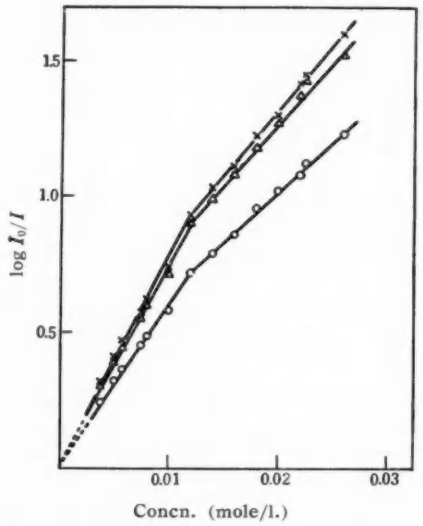


Fig. 1. Plot of absorbance (log I_0/I) *vs.* concentration in cyclohexane solution of dodecyl ammonium benzoate at 30±2°C. —△—, for 263 mμ; —×—, 270 mμ; —○—, for 276.5 mμ.

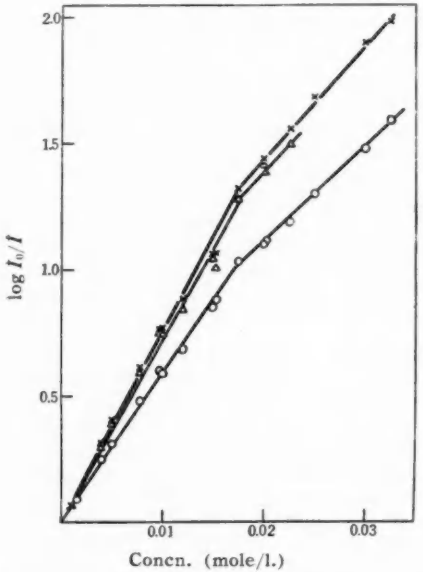


Fig. 2. Plot of absorbance (log I_0/I) *vs.* concentration in cyclohexane solution of octadecyl ammonium benzoate at 30±2°C. —△—, for 263 mμ; —×—, 270 mμ; —○—, for 276.5 mμ.

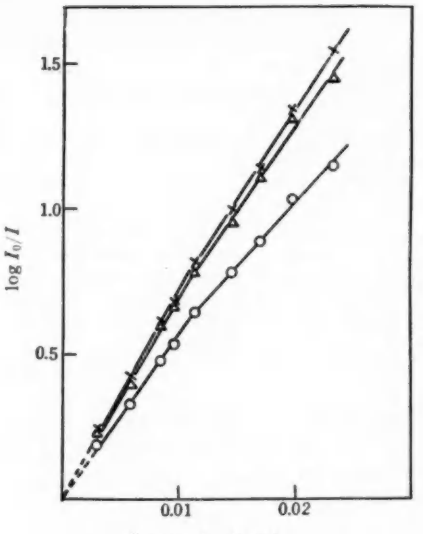


Fig. 3. Plot of absorbance (log I_0/I) *vs.* concentration in cyclohexane solution of dodecyl ammonium benzoate at 20±2°C. —△—, for 263 mμ; —×—, 270 mμ; —○—, for 277 mμ.

the peaks of 276 and 284 mμ[8]. No shifts were recognized in each absorption peak with varying concentration. The concentration dependence of the absorbance (log I_0/I) of each peak at 30 and 20°C was depicted in Figs. 1, 2 and 3. The concentration was described in terms of the molecular weight of a monomer of alkyl ammonium benzoate. It is readily recognized from the figures that the plots of the absorbance against the concentration consist of two linear parts within the concentration range studied in this experiment. This behavior was not very clear for the peaks of 263 and of 270 mμ of the solution of dodecyl ammonium benzoate at 20°C. The extrapolation of the linear parts of the lower concentration range passes the origin of the coordinates. That is, Beer's law is valid in this concentration range. It is, therefore, thought that the solute exists as monomeric molecule within this range. The break in this linear line at a certain concentration shows us that the state of the solute might be changed above this concentration. In the case of the cyclohexane solution of benzoic acid, no breaks appeared in the

8) H. E. Ungnade and R. W. Lamb, *J. Am. Chem. Soc.*, **74**, 3789 (1952).

TABLE I

CMC OBTAINED FROM SOLUBILIZATION (A) AND CONCENTRATION OF BREAK IN ABSORBANCE LINE (B)

		A (mole/l.)	B (mole/l.)
Dodecyl ammonium benzoate	30°C	0.012±0.002	0.012±0.001
〃 〃 〃	20°C	0.015±0.002	0.012±0.001
Octadecyl ammonium benzoate	30°C	0.014±0.002	0.018±0.001

TABLE II

THE VALUES OF ε_s, ε_m AND C_s (mole/l.)

	Dodecyl ammonium benzoate						Octadecyl ammonium benzoate		
Temperature	30°			20°			30°		
Wave length (mμ)	ε_s	ε_m	C_s	ε_s	ε_m	C_s	ε_s	ε_m	C_s
263	73_5	440	0.013	670	610	0.014	730	440	0.018
270	77_5	460	0.013	700	630	0.013	770	440	0.017
276.5-277	580	370	0.013	560	450	0.012	56_5	370	0.018

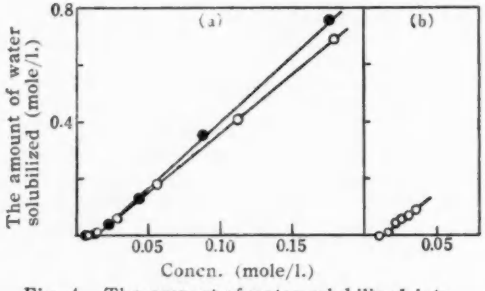


Fig. 4. The amount of water solubilized into the cyclohexane solution.
(a) —○—, for dodecyl ammonium benzoate at 30±2°C.
—●—, for dodecyl ammonium benzoate at 20±2°C.
(b) —○—, for octadecyl ammonium benzoate at 30±2°C.

absorbance lines for any peak of 276 and 284 mμ.

The relation between the limiting amount of water solubilized into detergent solutions and the concentration of detergent is shown in Fig. 4. It is seen in the figure that the relation is linear within the concentration range studied, though the linearity is somewhat ambiguous in the case of octadecyl ammonium benzoate because of its lower solubility. The concentration extrapolated to zero solubilization might be assumed to be the CMC[6]. The values of the CMC (A) obtained thus are listed in Table I. On the other hand, the concentrations corresponding to the break of absorbance lines (B), which are obtained from Figs. 1, 2 and 3 are also shown in the same table. The comparison of the values of B with the corresponding values of A shows us that both are in agreement with each other within the experimental error. Hence it will be reasonable to assume that the break in the absorbance line shows the initiation of micelle formation and that the concentration of the break is the CMC*. It will be, therefore, known that the measurement of the ultraviolet absorption spectrum has also ascertained the existence of the CMC.

Monomer Concentration: The equation $\log I_0/I=\varepsilon Cl$ may be used above the CMC. In this case, it is assumed that the overall extinction coefficient (ε) above the CMC can be expressed as follows:

$$\varepsilon=n_s\varepsilon_s+n_m\varepsilon_m, \quad (1)$$

where n is mole fraction and ε the extinction coefficient, subscripts s and m representing a monomeric molecule and a molecule participating in micelle formation. If the concentration of a monomeric molecule above the CMC is shown by C_s, $n_s=C_s/C$ and $n_m=(C-C_s)/C$, where C is the total concentration described in terms of the molecular weight of a monomer. Then formula (1) may be rewritten as follows:

$$\varepsilon C=\varepsilon_m C+C_s(\varepsilon_s-\varepsilon_m). \quad (2)$$

As seen in Figs. 1, 2 and 3 the linear relation is obtained between $\log I_0/I$ and C in the range above the CMC. Accordingly, ε_m can be estimated from the slope of the straight line above the CMC and $C_s(\varepsilon_s-\varepsilon_m)$ from the intercept on the ordinate by extrapolating it. ε_s is obtained from the slope of the linear part below the CMC. Hence C_s can be calculated. The values of ε_s, ε_m and C_s obtained for each absorption peak are tabulated in Table II.

* It was presented at the same Symposium by H. Sasaki, H. Okuyama and S. Saito of Osaka University that the extinction coefficient of cetyl pyridinium chloride in the aqueous solution begins to diminish sharply at the CMC.

ε_M is independent of the concentration as the result of the linearity of the absorbance curve above the CMC. As Harkins et al. pointed[2], the result just mentioned may be taken to indicate that the micelle size is constant in this range or that the transition probability of a molecule participating in micelle formation is not influenced by the micelle size. As the matter of course, the values of C_s are independent of the concentration and equal to the CMC from the assumption of the formula (1). This constancy of C_s corresponds to the case of higher aggregation of the results calculated from the law of mass action by Singleterry et al.[3] It is seen in Table II that the values of C_s obtained for separate peaks are all equal within the experimental error. This suggests that the assumption of the formula (1) might be reasonable. The effect of temperature on the CMC was recognized with difficulty in the case of dodecyl ammonium benzoate and of octadecyl ammonium benzoate at 20±2 and 30±2°C. The break has been observed in the absorbance-concentration relationship. On the other hand, the relation between the amount of water solubilized into solutions and the concentration of the detergent showed us the values of the CMC. The concordance found between the value corresponding to the break of the absorbance and the assumed CMC obtained from solubilization makes the existence of the CMC more probable. The concentration of the monomeric molecule and the molar extinction coefficient of the molecule participating in micelle formation were calculated with use of a simple assumption.

Summary

The concentration dependence of the absorbance for the ultraviolet absorption spectra was measured for cyclohexane solutions of dodecyl ammonium benzoate

The author wishes to express his hearty thanks to Mr. H. Tsubomura for the discussion on the results of the ultraviolet spectrum and to Professor H. Akamatsu for his kind encouragement.

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Department of Chemistry
Toho University, Narashino, Chiba

A Phase Transition Study on the Mercerization of Cellulose

By Yoshizo TSUDA

(Received February 18, 1957)

Introduction

The mercerization of native cellulose has been investigated by Sisson and Saner[1] with the X-ray method from a phase transitional point of view. The native cellulose contains a crystalline lattice of cellulose I, which is transformed into that of celluose II by the mercerization process. It is well known that the degree of transition depends on both the concentration and the temperature of sodium hydroxide solution used as the mercerizing agent. Furthermore, the concentration range depends also on the origin of the cellulose sample[2].

In a preceding paper[3] the present author has investigated the changes in the lateral order distribution of the native cellulose on the mercerization process and concluded that the lowering of the lateral order is induced with a concentration of sodium hydroxide lower than that required to induce the phase transition. But it is necessary to obtain correct knowledge about the phase transition in order to discuss the transition mechanism.

The main purpose of this investigation is to confirm the concentration range

1) W. A. Sisson and W. R. Saner, *J. Phys. Chem.*, **45**, 717 (1941).

2) B. G. Rånby and H. F. Mark, *Svensk Papperstidning*, **58**, 374 (1955).

3) Y. Tsuda and S. Mukoyama, This Bulletin, **30**, 271 (1957).

necessary to the transition and to obtain more information on the mercerization mechanism.

Experimental Procedure

a. Cellulose Samples.—Cotton linters pulp and sulfate and sulfite wood pulp were used. The analytical data of the samples were as follows:

(A) Cotton linters pulp, viscose grade, α-cellulose 98.3 %, degree of polymerization 610.

(B) Sulfate wood pulp, viscose grade, α-cellulose 94.3 %, degree of polymerization 690.

(C) Sulfite wood pulp, viscose grade, α-cellulose 95.7 %, degree of polymerization 1020.

b. Treatment with Sodium Hydroxide.—Before the treatment, the samples were disintegrated with a mixer, and then soaked at 20°C and 45°C in sodium hydroxide solution of various concentrations for two hours. The samples were recovered by suction on a glass filter, regenerated with 0.5 N acetic acid of the same temperature and washed with distilled water. The treated samples were dried with alcohol.

c. X-ray Diffraction.—The air dried samples, re-disintegrated with a mixer, were analyzed by Norelco Geiger counter-X-ray diffractometer (Copper K_α-radiation with Ni filter) with the specimen mounted by pressing in the specimen holder. The tubes were run at 35 kV. and with 15 mA emission current.

Measurement and Results

Figs. 1, 2 and 3 show the X-ray diffraction intensity curves of the untreated, completely mercerized and partially mercerized linters pulp respectively. The untreated linters pulp gives the pattern of cellulose I, the completely mercerized one that of cellulose II, and the partially mercerized one a mixed pattern of both. The absolute intensity of X-ray diffraction depends on the density of specimen pressed in the specimen holder, so that fluctuations of the absolute intensity in repeated measurements with the same sample were inevitable. Therefore it was impossible to utilize the absolute intensity itself to estimate the relative amounts of the two phases.

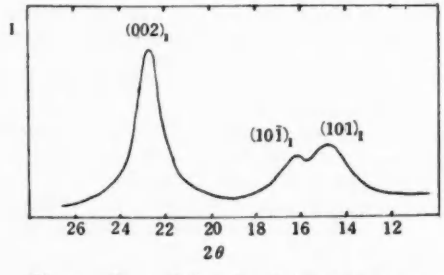

Fig. 1. X-ray diffraction intensity curve of the untreated linters pulp.

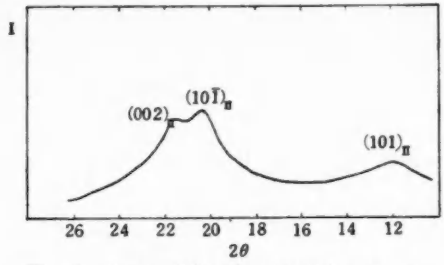

Fig. 2. X-ray diffraction intensity curve of the completely mercerized linters pulp.

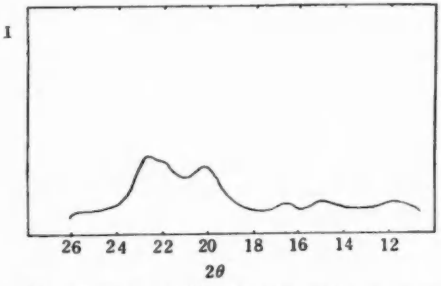

Fig. 3. X-ray diffraction intensity curve of the partially mercerized linters pulp.

In this experiment, to estimate the degree of the transition from cellulose I to cellulose II test experiments were made using samples containing known amounts of untreated and completely mercerized samples. The X-ray diffraction analyses of these samples were made with respect to the three pulp samples and then the degree of transition was followed taking the intensity ratio of (10$\bar{1}$) of cellulose II to (002) of cellulose I. In Figs. 4, 5 and 6 the

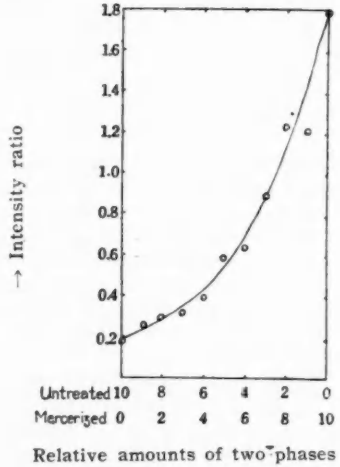

Fig. 4. Calibration curve for the linters pulp.

intensity ratio I $(10\bar{1})_{II}/I(002)_I$ is plotted against the relative amounts of the two phases. These calibration curves show that the gradient of curve increases with the increase in the amounts of cellulose I. Therefore it may be suggested that visual estimation of X-ray diffraction diagrams adopted by Sisson and Saner[1] leads to misunderstanding of the transition range. From the comparison of these figures it may be seen that the intensity ratio of the untreated linters pulp is lower than that for the untreated wood pulps, which is due to the higher lateral order of the native linters pulp.

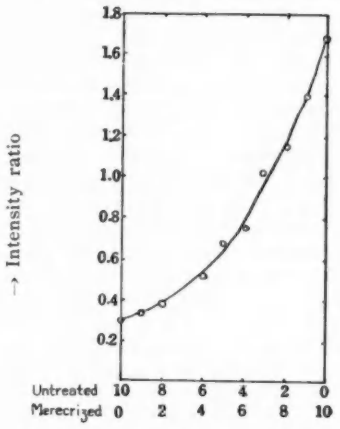

Fig. 5. Calibration curve of the sulfate pulp.

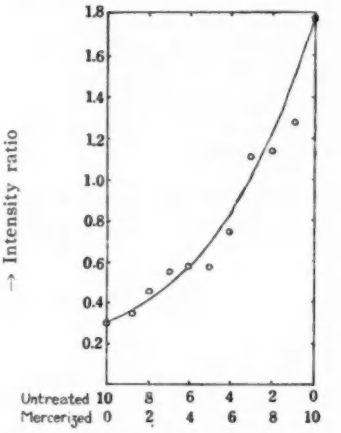

Fig. 6. Calibration curve of the sulfite pulp.

TABLE I
TRANSITION DATA OF SAMPLES TREATED AT 20°C

Linters Pulp			Sulfate Pulp			Sulfite Pulp		
NaOH[a] wt. %	I.R.[b]	D.T.[c] %	NaOH wt. %	I.R.	D.T. %	NaOH wt. %	I.R.	D.T. %
9.9	0.16	0	8.2	0.32	5	8.0	0.32	6
10.7	0.20	4	9.0	0.63	49	9.0	0.48	28
11.5	0.33	28	9.9	0.72	56	10.0	0.79	59
12.3	0.54	51	10.7	1.29	87	11.0	1.60	94
13.1	0.83	68	11.5	1.29	87	12.0	1.55	93
13.9	1.07	77	12.3	1.68	100			
14.6	1.23	82						
16.8	1.51	91						

TABLE II
TRANSITION DATA OF SAMPLES TREATED AT 45°C

Linters Pulp			Sulfate Pulp			Sulfite Pulp		
NaOH[a] wt. %	I.R.[b]	D.T.[c] %	NaOH wt. %	I.R.	D.T. %	NaOH wt. %	I.R.	D.T. %
10.0	0.21	8	9.0	0.28	0	9.0	0.30	0
11.0	0.26	16	10.0	0.38	18	10.0	0.36	12
12.0	0.31	25	11.0	0.58	44	11.0	0.74	54
13.0	0.33	28	12.0	1.07	75	12.0	1.04	72
14.0	0.56	52	13.0	1.13	78	13.0	1.40	86
15.0	1.18	81	14.0	1.25	83	14.0	1.63	96
16.0	1.38	87	15.0	1.56	95			
17.0	1.48	90	16.0	1.64	99			
18.0	1.59	94						

a) Concentration of NaOH used as the mercerizing agent.
b) Intensity ratio of I $(10\bar{1})_{II}$ to I $(002)_I$.
c) Degree of transition.

The observed intensity ratio and the corresponding degree of transition estimated from the calibration curves are tabulated in Table I and II.

In Fig. 7 and 8 the obtained degree of transition is plotted against the concentration of alkali. The main transition ranges are tabulated in Table III. As shown in Fig. 7 and Fig. 8, the higher resistance against the mercerization is characteristic of the linters pulp, whereas no difference between the sulfate and the sulfite pulp is observed in the transition behavior. The elevation of the temperature of the alkali treatment induces the increase in the concentration of the main transition range.

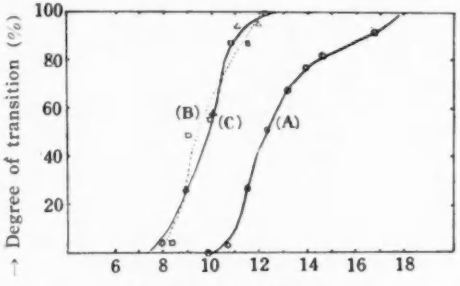

Fig. 7. Phase transition curves (at 20°C).
(A) the linters pulp
(B) the sulfate pulp
(C) the sulfite pulp

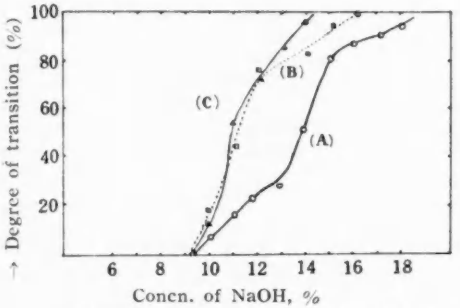

Fig. 8. Phase transition curves (at 45°C).

TABLE III
THE MAIN TRANSITION RANGE (EXPRESSED IN THE CONCENTRATION OF NaOH)

Pulp Samples	Temperature of Treatment	
	20°C	45°C
Linters Pulp	11–16	10–17
Sulfate Pulp	8–11	10–15
Sulfite Pulp	8–11	10–13

Discussion

The results reported here were based on the assumption that the decrystallization, which accompanies the mercerization, proceeds in proportion to the degree of transition. This assumption may contradict the results obtained in the preceding paper[3,4], but it must be mentioned that the pattern of cellulose II appears only for the sample whose cellulose II content is more than 40 per cent., according to the results of the test experiment. Therefore the decrystallization could not be discriminated from the phase transition by such an empirical method.

The transition range of the sulfate pulp is not different from that of the sulfite pulp, which is in good agreement with the lateral order distribution reported in the the preceding paper[4]. On the contrary, Ranby and Mark[2] reported that the sulfate pulp shows a higher resistance against the mercerization than the sulfite pulp. This difference may be due to the difference in the fine structure of both sulfate pulps. According to the results obtained here, it may be concluded that the crystalline structure of the sulfate pulp is not different from that of the sulfite pulp.

As shown in Fig. 8 all pulp samples show at 45°C an increased resistance against the complete mercerization. This tendency is in agreement with the results obtained by Sisson and Saner[1].

The variation in the lateral order distribution on the mercerization process which was reported in the previous paper[3] should be discussed again with the knowledge of transition obtained here. The variation range of lateral order distribution of the linters pulp at 20°C almost corresponds to the transition range obtained here, so that the preceding conclusion must be altered as follows: on the mercerization process the lowering of the lateral order is accompanied simultaneously with the phase transition; in other words, the former does not precede the latter. The misunderstanding of the transition range in the previous paper[4] was due to the visual estimation of the X-ray diffraction diagrams.

One may obtain further information on the mercerization mechanism, comparing the phase transition behavior with the the variation in the lateral order distribution acompanying it.

4) Y. Tsuda and S. Mukoyama, This Bulletin, **29**, 748 (1956).

Summary

The phase transition ranges were obtained at 20°C and 45°C for the linters pulp, the sulfate pulp and the sulfite pulp. It was concluded that the resistance of the linters pulp against the mercerization is higher than those of the wood pulp, where as no difference is observed between the sulfate and the sulfite pulp.

It was suggested also that the visual estimation of the X-ray diffraction diagrams may lead to a misunderstanding of the phase transition range.

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Research Department of
Toyo Rayon Co., Ltd.
Otsu, Shiga

Crystallinity Studies of Polychlorotrifluoroethylene by Infrared Method. I. Measurement of the Degree of Crystallinity

By Hiroshi MATSUO

(Received February 5, 1957)

Introduction

The measurement of the degree of crystallinity is becoming of increasing importance in the study of polymer properties. Therefore many methods for its estimation have been devised. The crystallinity of polychlorotrifluoroethylene (PCTFE) was studied by Price[1] by volume method, and by Hoffman[2] by specific heat method. It appears of interest to investigate the subject further by infrared method, which is also available for reliable estimation of crystallinity for a number of common polymers[3].

In the course of examination of infrared spectra of PCTFE, the author believed that they yield some bits information about the crystallinity and the state of the orientation. A survey of the spectrum revealed that some of the bands behaved as if they were given by the crystalline parts of the polymer, while others appeared to be produced by the amorphous parts. These discoveries were utilized in the present study of crystallinity of PCTFE, and the degree of crystallinity was estimated independent of other methods.

Effect of Crystallization on the Infrared Bands

PCTFE is an extremely intractable material, because there is no proper solvent at room temperature, and furthermore the spectrum of PCTFE shows such strong absorptions at about 1300–900 cm.$^{-1}$ region that thin films of 0.01–0.03 mm. thickness are necessary for infrared method. Thin films were prepared by extruding Daiflon[4] (NST 270) at above its melting point. The orientation of crystallites in the extruded film was estimated from the intensity distribution around the X-ray diffraction ring. It was examined further with a beam of polarized infrared radiation using a polarizer of silverchloride plates placed immediately in front of the entrance slit of the infrared spectrometer. A comparison of the spectra obtained when the electric vector was vibrating parallel and perpendicular to the extruded direction

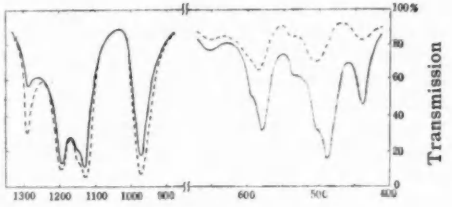

Fig. 1. Infrared spectrum of oriented polychlorotrifluoroethylene, obtained by polarized radiation.
——: electric vector parallel to the extruded direction.
----: electric vector perpendicular to the extruded direction.

1) F. P. Price, *J. Chem. Phys.*, **19**, 973 (1951).
2) J. D. Hoffman, *J. Am. Chem. Soc.*, **74**, 1696 (1952).
3) J. B. Nichols, *J. Appl. Phys.*, **25**, 840 (1954).

4) Trade name of high molecular weight PCTFE produced by Osaka Kinzoku Kogyo Co.

shows significant dichroism on the majority of absorption bands. This is shown in Fig. 1. These absorption bands indicated not only significant dichroism but also intensity changes as the crystallization proceeded[5]. The latter was examined comparing the spectra of annealed, quenched, and molten samples. In order to eliminate the effect of orientation, these samples were heated at above the melting point beforehand and then annealed or quenched to room temperature. Their spectra are shown in Fig. 2. To obtain the infrared spectrum

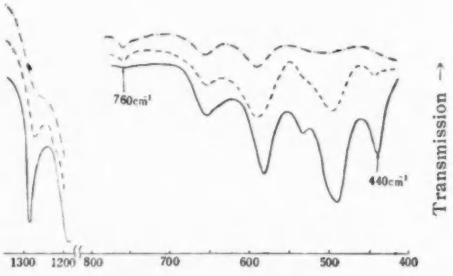

Fig. 2. Infrared spectra of polychlorotrifluoroethylene.
——: annealed sample,
----: quenched sample,
·-·-: molten sample at 230°C.

of molten polymer, a film of the polymer was sealed together with a thermocouple between potassium bromide plates. This was then placed in a heating cell[6] mounted on the spectrometer.

Fig. 2 shows that the absorption bands at 1290, 580, 506, 490 and 440 cm.$^{-1}$ increase markedly in intensity and present small shifts as the crystallization proceeds. This increase in intensity indicates that randomly oriented crystallites have been produced in the polymer by the heat treatment and it agrees with the results obtained by X-ray diffraction. These absorption bands whose intensities increase as the crystallization proceeds can be, therefore, regarded as crystalline bands. On the other hand, the intensity of the absorption band at 760 cm.$^{-1}$ decreases as crystallization proceeds, so that this band can be regarded as an amorphous band[7]. These crystalline and amorphous bands are summarized in Table I, where π means that

5) H. Matsuo, *J. Polymer Sci.*, **21**, 331 (1956).
6) R. E. Richards and H. W. Thompson, *Trans. Faraday Soc.*, **41**, 183 (1945).
7) R. G. J. Miller and H. A. Willis, *J. Polymer Sci.*, **19**, 485 (1956).

TABLE I
INTERPRETATION OF THE INFRARED SPECTRUM OF EXTRUDED PCTFE

Freq. cm.$^{-1}$	Relative Intensity	Dichroic ratio[a]	Character of band[b]	Probable assignment[c]
438	s	3.7	π c	CClF wagging
490	s	5.6	π c	CF_2 rocking
506	s		σ ? c	CF_2 bending
(535)			c	
580	s	2.2	π c	CF_2 wagging
658	m		π a ?	
723	w		π	
755	w		σ ? a	
972	vs		σ	CCl stretching
1130	vs		σ	CF_2 stretching
(1147)			σ	
1194	vs		σ	CF_2 stretching
1285	s	0.3	σ c	CF stretching

a) dichroic ratio $= \log(I_0/I)_\pi / \log(I_0/I)_\sigma$.
b) c = crystalline, a = amorphous.
c) These assignments are due to C. Y. Liang and S. Krimm, *J. Chem. Phys.*, **25**, 563 (1956).

the absorption in the case of the electric vector parallel to the extruded direction is greater than in the case of the perpendicular electric vector, and σ the reverse case.

Degree of Crystallinity

The degree of crystallinity was measured by the use of the crystalline band at 440 cm.$^{-1}$ and the amorphous band at 760 cm.$^{-1}$.

The experiments were carried out with a Perkin-Elmer Model 112 Spectrometer equipped with potassium bromide prism. The slit was driven connecting with wavelength drive cam, so as to obtain flat background trace. The resolving powers at 440 cm.$^{-1}$ and 760 cm.$^{-1}$ were approximately 3 cm.$^{-1}$ and 2.5 cm.$^{-1}$, respectively. Stray radiation at 440 cm.$^{-1}$ was less than one percent. of the detected radiation. The starting material was a sheet of melt-extruded, quenched film of 0.03 mm. nominal thickness. Samples with various degrees of crystallinity were obtained from it by quenching to room temperature from 230°C or annealing to various crystallization temperatures between 200° and 130°C. Specific volumes were obtained within the accuracy of ±0.0007 from densities measured by the flotation method at 25°C using a solution of bromoform and xylene. In

this case the optical density D was defined as follows,

$$D=(1/td)\log(I_0/I)$$

where t and d are the thickness and the specific gravity of the sample, I_0 is the height of the background trace obtained by the base-line method at the peak of the band, and I the height of the band peak. As the thickness of the sample had to be accurately measured for the optical density measurements, the following method was used. The portion irradiated by the infrared beam was cut out from the film, and weighed by a microbalance. The area of the surface of the film was determined by direct measurement. Density being known, the effective thickness could be calculated. The accuracy was estimated to be ±0.002 mm.

Since specific volume changes have been used to measure crystallinity, the changes in optical densities at 440 cm.$^{-1}$ and 760 cm.$^{-1}$ were correlated with change in specific volume. Specific volumes were plotted against optical densities for a number of samples. All points lie on a straight line within the accuracy of the experiment, and therefore the following equations were assumed.

$$D_1=K_1^c X+K_1^a(1-X)$$
$$D_2=K_2^a(1-X)$$

and consequently,

$$D_1=K_1^c-[(K_1^c-K_1^a)/K_2^a]D_2 \quad (1)$$
$$R=D_1/D_2=[X/(1-X)](K_1^c/K_2^a)+(K_1^a/K_2^a) \quad (2)$$

where X is the degree of crystallinity; D_1 and D_2 are optical densities at 440 cm.$^{-1}$ and 760 cm.$^{-1}$, respectively; K_1^c and K_1^a are extinction coefficients of crystalline and amorphous parts at 440 cm.$^{-1}$, respectively, and K_2^a is that of the amorphous part at 760 cm.$^{-1}$ R is the ratio of the observed absorbance at 440 cm.$^{-1}$ to that at 760 cm.$^{-1}$, and is independent of the thickness of the sample since the absorbances are determined for two bands in the same sample.

By plotting D_1 against D_2, a straight line was observed. Equation (1) means that the value of the inclination of the line corresponds to $(K_1^c-K_1^a)/K_2^a$ and the value of its intersection with the ordinate axis corresponds to K_1^c. Furtheremore, Equation (2) indicates that the value of R of the completely amorphous state correspond to (K_1^a/K_2^a). However, since the completly amorphous material could not be obtained by quenching the polymer from the molten state, the value of R of the completely amorphous state was determined by the following method. Daifloil[8] No. 50, which was a product of pyrolysed PCTFE and was a viscous liquid at room temperature, was used as an amorphous standard for the high molecular weight PCTFE. Its spectrum was very similar to that of the molten high molecular weight PCTFE, except for the existence of the absorption band at 1340 cm.$^{-1}$, which would be due to $=CF_2$ group[9]. Thus $R=2.05$ was obtained for completely amorphous polymer at room temperature. The same value of R was measured in the molten state which was obtained by heating Daiflon film to 240°C in the heating cell; it appears, therefore, that little change in the intensity of the absorption bands at elevated temperatures would be expected. Thus $K_1^c=9.02$, $K_1^a=2.12$, and $K_2^a=1.03$ were obtained, and the degree of crystallinity could be calculated from Equation (2):

$$X=(R-2.05)/(R+6.67) \quad (3)$$

The degree of crystallinity of PCTFE as a function of temperature was calculated from the measurement of R at various temperatures by the use of Equation (3). A film of 0.03 mm. thickness of the polymer which was quenched from above its melting point to room temperature, was inserted into the heating cell and degrees of crystallinity at various temperatures were measured. They are shown in Fig. 3. The sample was heated slowly to 100° then

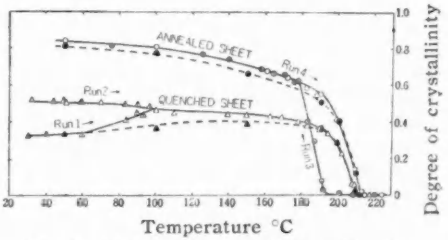

Fig. 3. Degree of crystallinity of polychlorotrifluoroethylene as a function of temperature.
(△) Run 1, (▲) Run 2 with quenched sample,
(⊗) Run 3, (○) Run 4 with annealed sample;
(▲, ●) obtained by Hoffman by specific heat method with quenched and annealed samples, respectively.

8) Trade name of low molecular weight PCTFE produced by Osaka Kinzoku Kogyo Co.
9) R. B. Barnes and R. C. Gore, *Anal. Chem.*, **20**, 402 (1948).

cooled down to room temperature (Run 1), and was heated again to 225° (Run 2). These data were listed in Fig. 3 as "quenched". The material was then cooled at a rate of 0.3°C/min. from 225° to room temperature (Run 3), and another run made to 225° (Run 4). These data were listed as "annealed". The degree of crystallinity of the quenched and the annealed sample obtained by the present method and that by Hoffman[2] by specific heat method agree with each other within ca. ±5%; this may be regarded satisfactory. Run 1 shows a definite increase in crystallinity of the quenched sample in the range of 80 to 100° as it is heated. This was confirmed further by the fact that the sample showed higher crystallinity than the original one when it was cooled from 100° to room temperature again. This definite increase must be due to super-cooled amorphous forming crystallites as the viscosity decreases sufficiently to permit recrystallization. On the other hand, the annealed sample apparently contains a few small crystallites which melt as low as 100°, and on further heating, the crystallinity steeply drops from about 196° and reaches zero at 212°. Between 180° and 212°, Run 3 and Run 4 do not coincide, and it may partly owe to non-attainment of equilibrium. The hysteresis shown by the non-coincidence of melting point (212°) and freezing point (195°) in this Figure was also observed in the measurements of specific volume, and dielectric constant and loss of PCTFE[10].

Furthermore, a linear relationship between the degree of crystallinity and the specific volume was obtained within the experimental uncertainty (Fig. 4). It leads to extrapolated values of 0.4901±0.001 and 0.4575±0.001 for specific volumes of completely amorphous and crystalline materials, respectively. Generally the degree of crystallinity can be also determined from specific volume method by the equation

$$X=(V_a-V)/(V_a-V_c)$$

However, so far as PCTFE is concerned, the value of specific volume for completely amorphous material (V_a) and that for completely crystalline material (V_c) have not as yet been determined with sufficient accuracy for computing absolute values of X, even by the extrapolation method of specific volume from the molten state[10,11] and by X-ray diffraction method[12]. Using

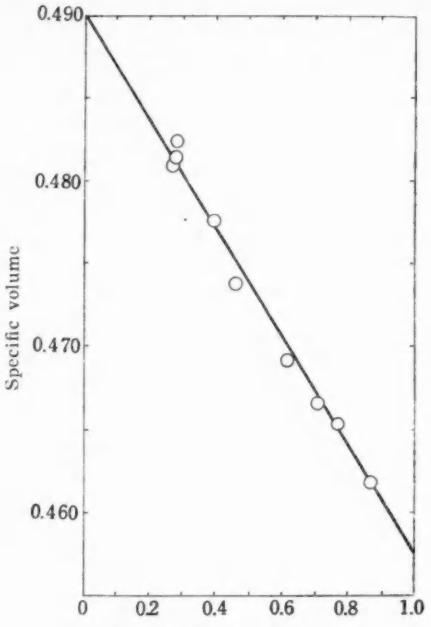

Fig. 4. Correlation of specific volume with degree of crystallinity of polychlorotrifluoroethylene.

V_a=0.4901 and V_c=0.4575 obtained by the present method, the degree of crystallinity was determined from the measurement of the specific volume V by the following equation,

$$X=(0.4901-V)/0.0326 \qquad (4)$$

In Table II, degrees of crystallinity obtained from infrared method and from specific volume method are shown. From this Table, it is apparent that amorphous material could not be obtained by such a quenching procedure of the molten polymer and the crystallinity of the quenched polymer attains to 27%, and, by annealing at higher crystallization temperature for several hours, the crystallinity of the annealed polymer amounts to 87%.

Summary

The crystalline-amorphous ratio, and consequently the degree of crystallinity of polychlorotrifluoroethylene was measured by use of the ratio of observed absorbance of crystalline band at 440 cm.$^{-1}$ to that of amorphous band at 760 cm.$^{-1}$. The crystallinity as a function of temperature was measured by this method, and it was in

10) F. P. Price, *J. Am. Chem. Soc.*, **74**, 317 (1952).
11) S. Furuya, *J. Polymer Sci.*, **20**, 587 (1956).
12) H. S. Kaufman, *J. Am. Chem. Soc.*, **75**, 1477 (1953).

TABLE II
PATICULARS OF SAMPLES OF PCTFE

Specific volume	Thickness mm.	log (I_0/I) at 440 cm.$^{-1}$	log (I_0/I) at 760 cm.$^{-1}$	R[a]	Crystallinity, % from I. R.[b]	Crystallinity, % from sp. vol.[c]	Condition of heat treatment
—	—	0.119	0.058	2.0	0	—	measured at 240°
0.4825	—	0.292	0.054	5.4	28	23	quenched from 230° to dry-ice temperature
0.4815	0.029	0.255	0.047	5.4	28	26	quenched from 230° to room temperature
0.4810	0.026	0.196	0.037	5.3	27	28	quenched from 230° to room temperature
0.4775	0.027	0.290	0.037	7.7	39	39	quenched film was heated at 130°
0.4739	0.030	0.310	0.033	9.4	46	50	quenched film was heated at 130°
0.4691	0.024	0.301	0.019	15.8	61	64	annealed from 230° to room temperature
0.4666	0.032	0.522	0.023	22.7	70	72	annealed from 230° to room temperature
0.4654	0.030	0.487	0.016	30.4	76	76	annealed from 230° to room temperature
0.4618	—	0.316	0.005	63.2	87	87	annealed at 190° for 3 hr.

a) $R = \log(I_0/I)440\,\text{cm.}^{-1} / \log(I_0/I)760\,\text{cm.}^{-1}$.
b) calculated from Equation (3).
c) calculated from Equation (4).

good agreements with that obtained by specific heat methd. Furthermore, a linear relationship between the degree of crystallinity and the specific volume was found, and it leads to extrapolated values of 0.4901 and 0.4575 for the specific volumes of completely amorphous and crystalline materials, respectively.

The author would like to express his appreciation to Mr. S. Owaki of this laboratory for X-ray diffraction work which has assisted in the interpretation of the data, and to Dr. Y. Kubouchi of Osaka Kinzoku Kogyo Co. for supplying Daiflon film and Daifloil No. 50.

Electrical Communication Laboratory
Nippon Telegraph and Telephone
Public Corporation
Musashino-shi, Tokyo

Microscopic Studies on Fused Catalysts for Ammonia Synthesis. V. Conversion Test with A and B Constituents and Some Studies on "M" Type Crystal

By Yoshio ŌSUMI and Makoto INOUE

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Introduction

As reported in our previous papers[1-9], it was shown, by the aid of the optical[1,5], the surface-electron[1,6] and the surface-ion microscopy[2,7], that some fused catalysts promoted with potash with or without some other additions, consisted of two different sorts of grain. Grains of the one sort (B), much less abundant and magnetic than those of the other sort (A), can be singled out magnetically from the finely pulverized catalyst. "B" powder is richer in potash than "A" powder. "A" powder possesses the magnetite lattice, while "B" powder shows a highly complicated "M"-type diffraction[3,8] pattern of lower degree of symmetry, probably owing to a slight modification of the magnetite lattice. "B" powder is less active than "A" powder towards decomposition of ammonia at the atmospheric pressure[1,9].

The present paper deals with the study on some properties of "B" powder and some comparative studies on "A" and "B" powder with respect to their reducibility in hydrogen, their corrodibility in acid, and their conversion activity and BET surface area in the reduced state.

"M" Type Phase

In ref. 3 it was shown that the content of the water-insoluble potash of A powder attained at most about 0.6 per cent., while that of "M" type "B" powder about five to ten times as much. The chemical analyses were performed after washing out soluble potash with cold distilled water. Recently the amounts of both the soluble and the insoluble potash have been redetermined with new samples. They were washed by boiling in water for one hour. The results are tabulated in Table I (No. II-1, II-4 and II-5) together with the previous ones (No. 3, 4, 10 and 12). The new results confirm the upper limit of potash content in "A" powder at about 0.6 per cent.

The potash content amounting to 0.6 per cent. in "A" powder corresponds to about one atom of potassium for every five unit cells of the magnetite lattice, whereas the potash content in "B" powder about one to two atoms of potassium for each unit cell of the "M" type lattice which is assumed to be equal to that of magnetite.

It is a laborious task to magnetically separate "B" powder from "A" powder. It was attempted to obtain a nearly pure "B" mass by adding as much as 5 per cent. of potash in the usual process of preparing the catalyst. Catalyst II-4 thus prepared gave, however, on magnetic separation, only a small portion of "B" powder comparable in amount with ordinary catalysts. The greater part of potash was found water soluble (Table I).

Of twelve sorts of catalyst previously examined by X-rays, those promoted with potash and alumina always contained "B" powder of the "M" type in which iron is largely in the ferric state. The "B" powder from catalyst II-1 (Table I), however, gives the FeO pattern, instead of the "M" and in fact the iron in it is found mainly in the ferrous state, while the iron in the "A" powder has the usual magnetite composition. The insufficient oxidation of the catalyst in the fusion process seems to affect the oxidation state of iron in the "B" phase rather than in the "A". This fact suggests that the presence of

1) N. Sasaki and Y. Ōsumi, *J. Chem. Soc., Japan (Pure Chem. Sec.)* **73**, 808 (1952).
2) Y. Ōsumi, ibid., **74**, 308 (1953).
3) Y. Ōsumi, This Bulletin, **26**, 519 (1953).
4) Y. Ōsumi, ibid., **28**, 156 (1955).
More details of the results are found in 5) etc.
5) Y. Ōsumi, *Ammonium Sulfate Engineering* (Japanese), **16**, 13 (1952).
6) Y. Ōsumi, ibid., **17**, 8 (1953).
7) Y. Ōsumi, ibid., **18**, 11 (1953).
8) Y. Ōsumi, ibid., **18**, 14 (1953).
9) Y. Ōsumi, ibid., **23**, 6 (1954).

TABLE I

Catalyst No. and (promoter in per cent)	species of powder isolated	weight per centage	X-ray diffraction pattern	per centage of oxide found in the powder							
				K_2O			CaO	MgO	Al_2O_3	Fe-oxides*	T_c°C
				water soluble	water insoluble	total					
II-1	A	99.0	magnetite	0.4	0.5	0.9	0.5		4.2	94.1	530
(1 K_2O, 1 CaO, 5 Al_2O_3	B	1.0	FeO	0.8	0.9	1.7	1.1		5.6	89.0	465
II-4	A	89.8	magnetite	3.0	0.6	3.6			5.1	90.8	550
(5 K_2O, 5 Al_2O_3)	B	10.2	M	6.8	3.1	9.9			6.0	82.5	550
II-5	A	90.5	magnetite	0.2	0.6	0.8	0.3		5.3	94.1	515
(1 K_2O, 1 CaO, 5 Al_2O_3)	B	9.5	M	0.7	5.4	6.1	1.0		4.4	90.4	505
3	A	96.1	magnetite		0.58					—	—
(1 K_2O)	B	3.9	FeO		2.13					—	—
4	A	96.9	magnetite		0.40				4.8	92.8	510
(1 K_2O, 5 Al_2O_3)	B	3.1	M		4.00				6.3	84.5	515
10	A	95.0	magnetite		0.52		0.46		11.3	84.4	520
(1 K_2O, 1 CaO, 10 Al_2O_3)	B	5.0	M		3.49		2.41		25.0	71.6	515
12	A	92.0	magnetite		0.34			0.70	4.9	93.7	515
(1 K_2O, 1 MgO, 5 Al_2O_3)	B	8.0	M		1.98			0.61	3.4	93.1	515

* These figures are obtained by conveniently assuming all Fe exists as Fe_3O_4 in "magnetite", as Fe_2O_3 in "M" and as FeO in "FeO". Actually, for example, $Fe^{2+}/Fe^{3+}=36/67$ for Cat II-1, A ("magnetite" type), $Fe^{2+}/Fe^{3+}=9/91$ for Cat II-4, B ("M" type) and $Fe^{2+}/Fe^{3+}=71/29$ for Cat II-1, B ("FeO" type).

alumina is not sufficient for the formation of the "M" type "B" phase and the state of oxidation of iron is rather essential. It may be that alumina is even unnecessary in this connection and the formation of the "FeO" type instead of the "M" type in ctalyst 3 (Table I) is a result of the insufficient oxidation and not of the absence of alumina.

Attempts have been made to synthesize the oxide having the "M" type structure by heating,in an iron boat in nitrogen

TABLE II

THERMOSTABILITY OF B POWDER ("M" type)

temperature C°	period of heating hr.	X-ray diffraction pattern	T_c°C
550	1	"M", (Hematite)	
750	1	"M", (Hematite)	505
880	1	"M", Hamatite	
960	1	Hematite, "M"	500
1000	2	"M", Hematite	
1040	1	"M", Hematite, Magnetite	
1130	1	Magnetite, Hematite, "M"	520
1220	1	Magnetite, Hematite	
1340	2	Magnetite, (Hematite)	540

X-ray figures are listed in the order of decreasing intensity and braketed ones are very weak.

TABLE III

POTASH FUSION OF IRON OXIDE

temperature C	type of oxide	X-ray diffraction pattern
700	Fe_3O_4 Fe_2O_3	Magnetite, "M" "M"?
880	Fe_3O_4 Fe_2O_3	"M", Magnetite "M"?, (FeO)
930	Fe_3O_4 Fe_2O_3	"M", Magnetite Magnetite, FeO
1010	Fe_3O_4 Fe_2O_3	FeO, Magnetite, FeO FeO
1200	Fe_3O_4 Fe_2O_3	Magnetite, FeO FeO Magnetite

Each oxide was fused with potassium nitrate of half the weight of the oxide for three hours in a nitrogen stream.

atomosphere, at temperatures given in Table III, a certain quantity of pure magnetite or hematite with half the weight of potassium nitrate and without any addition of alumina. The X-ray examination of specimens after washing with water shows that the "M" type structure can be obtained when the heating temperature was not higher than 1000°C. The conclusion is that for the synthesis of "M" phase the excess of potash alone is necessary, alumina and other additions being unessential. The "M" particles thus synthesized, however, are not at all attracted by the magnet while the "M" type

"B" particles are feebly attracted.

Further attempts were made to synthesize the "M" type crystals containing alumina by potash fusion of mixtures of magnetite and alumina in more or less intimate mixture (Table IV). The structure aimed at was obtained in products fused at about 900°C with a sufficient quantity of potash (the products were also non-magnetic).

The following experiments were performed with "A" and "B" powders prepared from catalyst II-5 (Table-I) with alumina, lime and potash as promoters.

Thermostability of the "M" type Phase

The thermostability of the "M" type lattice mentioned above was tested as follows. About 0.5 g of B powder placed on a piece of platinum plate was heated in a porcelain tube in the nitrogen stream at temperatures given in Table II and after cooling subjected to the X-ray examination. Table II shows that the "M" type phase becomes unstable at about 1000°C, to change into the magnetite lattice (the powder becomes strongly magnetic). This change is probably caused by the loss of potash and oxygen at high temperatures so that the "M" type phase can survive much higher temperatures when it cools down from the solidifying point as the constituent in the matrics of the "A" phase. It will be noted in this connection that the electron-emission characteristics of "B" grains as revealed by the surface electron microscope[1] may be related to the potash liberated accompanying this lattice transformation.

As to the possible mechanism of the formation of the "M" type phase in fused catalysts, it may be suggested that at higher temperatures fused oxide probably forms a homogeneous phase with potash, which on solidifying yields magnetite crystals with about 0.6 per cent. of potash, the remaining potash being enriched at the crystal boundaries to form "M" type crystals.

Corrosion in Acid Solutions and Reduction in Hydrogen Gas

The change in appearance of the polished surface of "B" grains, as the optical microscope observations showed[1], was less marked on reduction in hydrogen and more marked on attack in hydrochloric acid than that of "A" grains. But the loss in weight in both cases of "A" powder does not differ much from that of "B" powder.

The action of the acid was observed with 1.5 g of the specimen by dipping in hydrochloric acid at room temperature. In 1 N-acid dissolved 6 per cent. of both "A" and "B" in one day, and in 6 N-acid 17 per cent. of A and 15 per cent. of "B" in three hours.

The weight change during reduction in hydrogen was followed with a quartz fiber torsion balance carrying 0.1 g. of the specimen in powder form (~200 mesh) in a heated tube through which hydrogen gas at atmospheric pressure was passed at the rate of 40 cc. per minute. The temperature was raised at the rate of 100°C per 40 minutes.

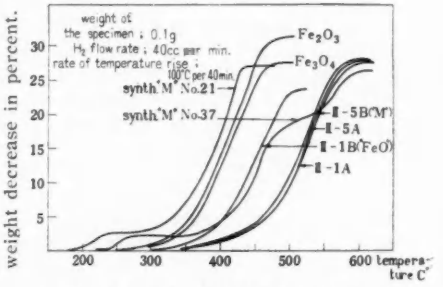

Fig. 1. Rate of weight decrease by hydrogen reduction for A, B powder and some other iron oxides.

The reduction curve of "B" (Fig. 1) is nearly the same in form as that of "A". The temperature T (Table I) at which half the oxide has been reduced to iron is almost the same for "A" and "B" powders from one and the same catalyst. Different values of T were obtained for catalyst II-1, whose "B" powder shows the FeO pattern.

It is a matter of well-established fact[1,5,10] that alumina in magnetite raises the temperature of beginning reduction. It may, therefore, be concluded that the aluminium atoms in the "M" type lattice are situated essentially in the same manner as in the magnetite lattice. But the T values of those "M" type products (No. 37 and 43 in Table IV) prepared by potash fusion of alumina-promoted magnetite are lower than that of the "M" type "B" powder separated from catalysts. This fact may be explained by the assumption that the excessive potash

10) A. Mittash u. E. Kennecke, Z. Elektrochem., 38, 666 (1932).

TABLE IV

POTASH FUSION OF IRON OXIDE WITH ALUMINA

No. of specimen	temperature °C	materials and mixing ratio in brackt		X-ray diffraction pattern	T_c °C
21	850	Fe_3O_4(10) Al_2O_3(0.5)	KNO_3 (5)	"M"	395
22			KOH (5)	"M"	425
23			K_2CO_3 (5)	FeO	410
34	520	catalyst promoted with 5% Al_2O_3 (10)		Hematite	490
35	610			Hematite	485
36	730		KNO_3 (5)	Hematite	465
37	900			"M"	465
79	970			FeO	425
39	900	catalyst promoted with 5% Al_2O_3 (10)	KNO_3 (0.5)	Hematite	490
42			KNO_3 (1)		490
43			KNO_3 (2)	"M"?	490
41			KNO_3 (5)		480
58	700	catalyst promoted with 5% Al_2O_3 (10)			480
59	810			Hem, Mag	480
60	900		K_2CO_3 (3)		485
77	1000			FeO	470
73	1150			FeO	465
52	900	catalyst promoted with 5% Al_2O_3 (10)	K_2CO_3 (0.2)		480
53			K_2CO_3 (0.7)	Mag, Hem	475
56			K_2CO_3 (2)		460
57			K_2CO_3 (5)	Magnetite	450

Specimens were fused for about three hours in air.

during the fusion process has extracted alumina from magnetite to form potassium aluminate.

Measurements of Conversion Activity and BET Isotherms

Seven g. of "A" (or "B") powder were pressed into small tablets, 3 mm. in diameter and 3 mm. high, and sintered at about 700°C in nitrogen stream. At this temperature the disintegration of the "M" type crystal does not occur. The tablets were placed in a layer, 18 mm. thick and 18 mm. in diameter, in the convertor shown in Fig. 2, and following a fixed schedule (Table V) reduced in hydrogen stream at

TABLE V

REDUCTION SCHEDULE FOR CONVERSION TEST

temperature °C	reduction period, day	amount of water caught in the trap placed at the outlet of the converter, g	
		A	B
250	1/4		
275	1/4	0.275	0.241
300	1/2		
325	1	0.779	0.676
325	1	0.500	0.253
325	1	0.260	0.277
350	1	0.207	0.404
375	1	0.100	0.275
400	1/2		
425	1/4	0.088	0.172
450	1/4		
total	7	2.209	2.298

The trap was kept at dry-ice temperature.

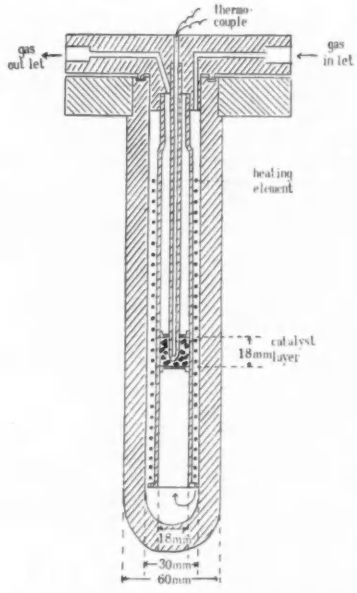

Fig. 2. Experimental convertor.

atmospheric pressure at the space-velocity of about 15000. Hydrogen was purified by being passed through a nickel catalyst, potassium hydroxide and phosphorus pentoxide. The progress of reduction was followed roughly by weighing at intervals the water captured from the issuing hydrogen gas in a trap cooled at −78°C(Table V).

For the conversion tests hydrogen and nitrogen from 150 atm. cylinders were mixed in the ratio of 3 : 1 in a gas holder, and passed over a copper catalyst and compressed into a storage vessel at 100 atm. pressure. For the conversion test at ordinary pressure the raw gas mixture from the storage vessel was reduced to

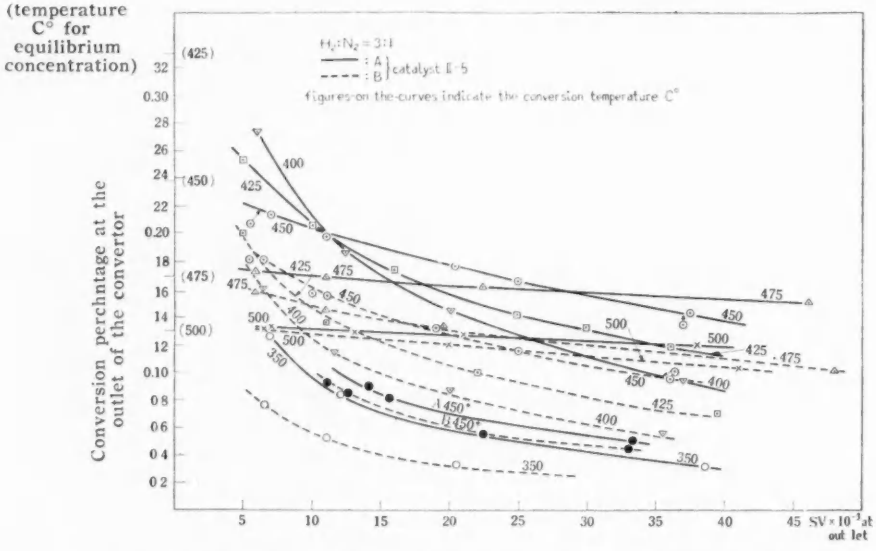

Fig. 3. Conversion activities of A and B powder at atmospheric pressure.
* These curves of low activities were obtained after the experiment of high pressure conversion

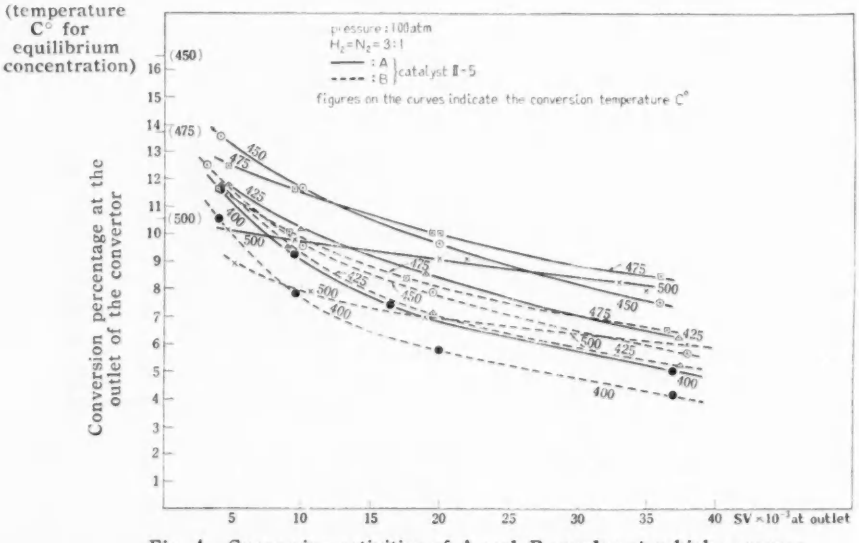

Fig. 4. Conversion activities of A and B powder at a high pressure.

atmospheric pressure and purified in the same way as for the reduction test. For the higher-pressure conversion test, the raw gas at 100 atm. was passed over a nickel catalyst and led through silica-gel and alumina-gel for dehydration.

The results represented in Figs. 3 and 4 clearly show that the conversion activity of "B" powder is lower than that of "A" powder for the whole range of space velocity and particularly at low temperatures.

The influence of water vapor upon the activity was tested by passing the raw gas through a water saturator kept at 0°C. The results (Table VI) show that the water vapor has a similar poisoning effect on the conversion activity as on the decomposition activity at ordinary pressure.

In order to investigate the surface condition of "A" and "B" powders after reduction, BET measurements were carried out by using carbon dioxide and carbon monoxide. Brunauer and Emmett[11,12] state that at the first stage of adsorption at −78°C a rapid chemisorption of carbon dioxide occurs on the surface alkali molecules, followed by the usual physical adsorption on the whole surface (the "total" isotherm).

Seven g. of "A" or "B" powder were reduced in the adsorption bulb made of pyro-glass (about 10 cc.) following the same reduction schedule in the conversion test. Fig. 5 represents adsorption isotherm of carbon dioxide at −78°C on "A" and "B" powders. The isotherm designated as "van der Waals" was obtained at −78°C with the sample outgased for one hour at 0°C after the "total" isotherm measurement. At this temperature all carbon dioxide molecules adsorbed physically are to be removed without the chemisorption being affected, so that from the difference between the two isotherms the amount of chemisorbed carbon dioxide "V_c" may be obtained, while from the van der Waals isotherm the amount of the gas forming the monomolecular layer "V_m". Since "V_m" values for "A" and "B" powders are essentially equal, the total surface of the iron crystallites formed by the reduction seem to be almost the same for the two types of oxides. From "V_c" and "V_m" values we obtain the coverage by the alkali molecules amounting to about 86 per cent. of the total surface for "B" and 58 per cent. for "A" powder. The difference is apparently not great enough to account for the large difference in the potash content.

After evacuation for about one day at

TABLE VI

EFFECT OF WATER VAPOR ON CONVERSION ACTIVITY AT 450°C, 100 ATOM AND S.V.: 23000

	percentage of NH_3 in the outlet gas	
	A	B
Pure gas	9.2	7.5
Gas containing H_2O	2.0	0.5

Gas was bubbled through water saturator kept at 0°C.

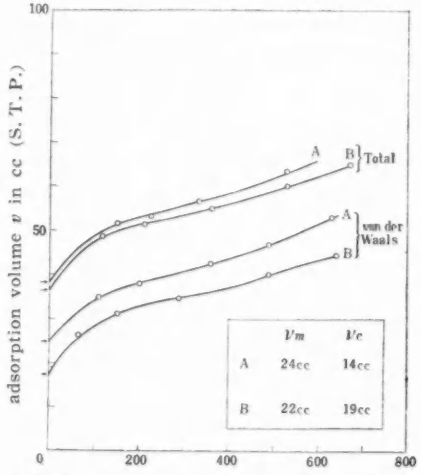

Fig. 5. Adsorption isotherms for carbon dioxide at −78°C on A and B powder.

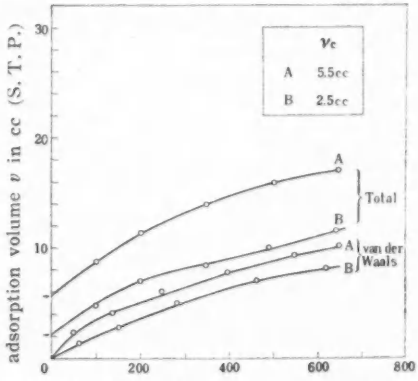

Fig. 6. Adsorption isotherms for carbon monoxide at −78°C on A and B powder.

11) P. H. Emmett and S. Brunauer, *J. Am. Chem. Soc.*, **59**, 310 (1937).
12) Idem., ibid. **59**, 1553 (1937).

400°C, adsorption isotherms were determined with carbon monoxide which is adsorbed on the metallic iron surface only[7,8]. The isotherm may more or less be affected by the carbon dioxide still remaining on the iron surface. Fig. 6 shows that the area of the iron covered surface is smaller for "B" than for "A". The sum of the potash-covered and iron-covered areas is nearly equal to the total area ("V_m") for "B" powder, but smaller for "A" powder. This probably is, as Brunauer and Emmett suggested, due to the occupation of the iron surface by alumina.

Summary

Iron synthetic ammonia catalyst (No. II-4) promoted with aluminium oxide, potassium oxide and calcium oxide was separated magnetically into two different sorts of powder, "A" with magnetite structure and "B" with "M" type structure. As to their catalytic activities for normal and high pressure conversion at temperatures between 400 and 520°C, it was found that "B" was less active than "A" particularly for the low temperature conversion. Some other properties of these powders are as follows:

(1) "B" powder becomes unstable when heated above 1000°C and changes into magnetite. Powder with the lattice structure of "M" type can be synthesized by sintering iron oxide at about 900°C with a sufficient amount of potassium nitrate or hydroxide, but it is completely non-magnetic.

(2) "A" and "B" powder showed almost equal rate of weight decrease when reduced in hydrogen gas or treated with acid solutions.

(3) The BET measurement carried out with "A" and "B" powder reduced in hydrogen revealed that the total specific surface area is almost equal for both "A" and "B" whereas the portion occupied by alkali molecules is larger for "B" powder.

We owe our deep gratitude to Dr. A. Uchida, Tokyo Industrial Research Institute for providing us with Cat. II-5 in this study and also to Mr. Z. Ujino in our Laboratory for his help in chemical analysis.

Mitsubishi Kasei Laboratory
Kawasaki, Kanagawa

Existence of Nitrous Oxide in Gases Produced from Nitrogen Compounds Decomposed by the Strong Phosphoric Acid-Iodic Acid Method

By Shigeru OHASHI, Yuzi TAKAYAMA*, Hiroshi HIGASHIDANI and Sachiko TAKI

(Received February 16, 1957)

In the previous papers[1] one of the authors presented a new method for the determination of nitrogen in nitrogen compounds. The compounds such as amines and ammonium salts are decomposed by heating with a mixture of strong phosphoric acid and potassium iodate to liberate the nitrogen contained in them. By sending the liberated nitrogen with carbon dioxide into an azotometer filled with a concentrated solution of potassium hydroxide, the nitrogen can be determined gas-volumetrically.

In the first course of this investigation, the gases accumulated in the azotometer by the procedure described above were considered as molecular nitrogen. However, it was found that amounts of liberated iodine[2] by the above reactions always exceeded the theoretical ones which were

* Mitsubishi Rayon Co. Ltd., Tokyo.

1) S. Ohashi, This Bulletin, **28**, 177, 537 (1955); **29**, 700 (1956).

2) For the experimental details, cf. S. Ohashi, This Bulletin, **28**, 171 (1955).

TABLE I

IODINE LIBERATED BY THE DECOMPOSITION OF NITROGEN COMPOUNDS WITH STRONG PHOSPHORIC ACID IODIC ACID

Compound	Sample taken mg.	I_2 found mg.	I_2 calcd. as N_2 mg.	I_2 calcd. as N_2O mg.	N_2O %
Ammonium Sulfate	102.6	136.0	118.3	157.3	44.9
,,	102.6	134.1	118.3	157.3	39.8
,,	102.6	138.0	118.3	157.3	49.4
,,	205.2	263.6	236.6	316.0	33.7
Acetanilide	15.7	116.4	115.0	117.9	75.0
,,	17.8	132.6	130.4	133.8	80.5
,,	24.3	179.9	178.0	182.5	74.4
,,	29.0	212.8	212.4	218.0	57.9
Urea	22.6	69.2	57.3	76.4	61.7
,,	39.1	118.1	99.2	132.2	57.2
,,	51.5	155.1	129.6	172.8	56.2
,,	71.5	228.2	181.3	242.0	77.8
Glycine	19.5	64.7	59.3	65.8	90.4
,,	29.9	97.8	91.0	101.1	86.0
,,	32.5	106.8	98.9	110.0	86.1

Reaction temp. below 240°C

TABLE II

ANALYSES OF NITROGENOUS GASES BY MASS SPECTROMETER

Compound	Sample taken	Composition of gases				$N_2O/(N_2+N_2O)$
		CO_2	N_2	N_2O	O_2	
	mg.	%	%	%	%	%
Ammonium sulfate	15	95.6	2.8	1.6	0	36
Acetanilide	33	98.4	0.5	1.0	0	65
Urea	25	97.1	0.4	2.2		82

Reaction temp. 233°C

calculated on the assumption that the nitrogen in the sample would be changed into molecular nitrogen. The data obtained for several nitrogen compounds are shown in Table I. The discrepancy between the observed and the calculated amount of iodine may be due to the fact that the nitrogen in the samples has not been converted into molecular nitrogen alone, but partly changed into nitrous oxide. For example, if molecular nitrogen is produced from urea by the oxidation with iodic acid, 3 mol. of iodine will be liberated from 5 mol. of urea.

$$5CO(NH_2)_2+6HIO_3 = 5CO_2+13H_2O+5N_2+3I_2$$

And if nitrogen oxide is produced from it, 4 mol. of iodine will be liberated from 5 mol. of urea.

$$5CO(NH_2)_2+8HIO_3 = 5CO_2+14H_2O+5N_2O+4I_2$$

In Table I all the found values of iodine are between those calculated from the two equations mentioned above, respectively. It indicates that the nitrogen in the sample may be converted into both molecular nitrogen and nitrous oxide. The contents of nitrous oxide in the gases calculated from the amounts of liberated iodine are also shown in Table I.

Since the evidence described above is still an indirect one for the existence of nitrous oxide in the gases, then in order to obtain direct evidence, the gases, produced by the decomposition of some nitrogen compounds with the mixture of strong phosphoric acid and potassium iodate, were swept into a gas reservoir with a flow of carbon dioxide and analyzed by a mass spectrometer. Although both nitrous oxide and carbon dioxide indicate the peak of M/e 30 in their mass spectra, the peak height due to carbon dioxide was much less than the observed one. Thus the existence of nitrous oxide was verified and its contents in the gases were determined[3]. The results of the analyses for

3) Cf. Y. Takayama and S. Ohashi, This Bulletin, **30** 606 (1957).

ammonium sulfate, urea, and acetanilide are shown in Table II. It is clear that the gases from these compounds contain both nitrogen molecule and nitrous oxide and the latter takes about 30 to 80 % of the total nitrogenous gases.

In connection with the above results, the present authors doubted whether gases produced from nitrogen compounds by the Dumas' method are truly nitrogen molecule or not. Therefore isonicotinic acid, 2-methyl-5-vinyl-pyridine polymer, and β-dimethylamino-acetaldehyde-dimethylacetal were decomposed by the normal Dumas' method, in which a flow rate of carbon dioxide was about 6.7 ml./mm., and the gases produced were analyzed by the mass spectrometer. Also in the case of the Dumas' method, the existence of nitrous oxide was pointed out, but its amount was much less than that in the case of the strong phosphoric acid-iodic acid decomposition method.

Full details will be published in the near future.

Department of Chemistry, Faculty of Science, Kanazawa University
Kanazawa

Decomposition of Pyridine Compounds with Strong Phosphoric Acid-Iodic Acid: Some Information Obtained By Mass Spectrometry

By Yuzi TAKAYAMA and Shigeru OHASHI*

(Received February 16, 1957)

In the previous investigations[1] on the determination of nitrogen in organic compounds by the strong phosphoric acid-iodic acid decomposition method, satisfactory results were obtained for analyses of ammonium salts, amines, azo-compounds, pyrroles, thiazoles, nitro and oxime compounds, etc., but pyridine compounds did not give any good results and the reason for this was uncertain. The present investigation was undertaken to discover the reason and to find out a clue for extending this new analytical method to pyridine compounds. Particularly, for analyses of gases produced by the decomposition of nitrogen compounds, a mass spectrometer was employed effectively.

Several nitrogen compounds were decomposed with a mixture of strong phosphoric acid and potassium iodate at various temperatures, gases produced were swept into a gas reservoir with a flow of carbon dioxide, and then the gases analyzed by the mass spectrometer. On the other hand the sum of volumes of molecular nitrogen and nitrous oxide[2] obtained by the above procedure were compared with the theoretical ones. These results are shown in Table I. An example of analysis of a mass spectrum is illustrated in Table II.

A standard mass spectrum of each gas component anticipated was, of course, previously taken. Since the peak of m/e 22 in a mass spectrum is a characteristic one for carbon dioxide and it does not appear in spectra of the other components, each peak height due to carbon dioxide was calculated from the standard spectrum of pure carbon dioxide and the observed peak height of m/e 22. These are shown in the column 3 of Table II. By deducting the peak heights of carbon dioxide thus calculated from the initially observed peak heights, respectively, peak heights Δ_1 which are due to the other components than carbon dioxide were obtained. As in the peak heights of Δ_1 the peak of m/e 30 is produced only by the presence of nitrous oxide, the peak heights due to nitrous oxide were calculated in a similar way and so on.

* Department of Chemistry, Faculty of Science, Kanazawa University Kanazawa.

1) S. Ohashi, This Bulletin, **28**, 177, 537 (1955); **29**, 700 (1956).

2) Cf. S. Ohashi, Y. Takayama, H. Higashidani and S. Taki, This Bulletin, **30**, 604 (1957).

TABLE I

COMPOSITION OF GASES IN THE GAS RESERVOIR

(mol. %)

10 ml. of strong phosphoric acid and 600 mg. of potassium iodate were used in each analysis. The final reaction temperatures were kept for eight min.

Compound	Sample taken	Final reaction temp.	Reservoir volume	CO_2	N_2O	N_2	O_2	(N_2+N_2O) found	(N_2+N_2O) calcd.
	mg.	°C	ml.	%	%	%	%	ml.	ml.
Isonicotinic acid	20	233	125	ca. 100	0	0	0	0	1.9_5
〃	〃	253	113	97.8	1.0_1	0.8_5	0.3_8	2.1_0	,,
〃	〃	275	125	97.5	0.7_8	0.8_0	0.9_7	1.9_8	,,
Poly-2-methyl-5-vinyl-pyridine	〃	233	113	ca. 100	0	0	0	0	2.0_5
〃	〃	260	113	98.2	0.4_4	0.1_7	0.4_1	1.8_2	,,
Polyacrylonitrile	28	233	125	97.4	1.5_3	1.2_5	0	3.4_8	3.4_7
Acetanilide	33	233	125	98.4	1.0_2	0.5_5	0	1.9_8	1.7_6
Urea	25	233	113	97.1	2.2_0	0.4_8	0	3.0_5	3.2_0
Ammonium Sulfate	15	233	125	95.6	1.6_0	2.8_0	0	5.5_0	5.4_5

TABLE II

ANALYSIS OF MASS SPECTRUM

Sample: Isonicotinic acid 20 mg. Final reaction temp.: 275±2°C
Date: Oct. 25, 1956, No. 4. *n*-Butane m/e 43: 58.99
Magnetic current: 0.25 amp. Ionic current: 12.5 μ amp.
Scanning voltage: 3550 V. Sample pressure: 44.53 μ Hg.

M/e	peak height found	CO_2	J_1	N_2O	J_2	O_2	J_3	N_2	J_4
14	5.4	0.9_2	4.4_8	1.9_6	2.5_2		2.5_2	2.2_4	0.2_8
16	236.6_7	240.7_1	-0.40_6	0.6_9	-4.7_5	0.3_3	-5.0_8		-5.0_8
18	0.8								0.8
22	36.8	36.8	0						0
28	260.5	242.9_9	17.5_1	1.7_2	15.7_9	0.9_2	14.8_7	14.8_7	0
30	5.0	0.5_5	4.4_5	4.4_5	0				0
32	15.8	0.6_8	15.1_2		15.1_2	15.1_2	0		0
44	2123.7	2117.3_5	6.3_6	11.1_7	-4.8_1				-4.8_1
46	8.9	8.7_9	0.1_7	0.0_2	0.0_9				0.0_9

As indicated in Table I it was disclosed that pyridine compounds such as isonicotinic acid and poly-2-methyl-5-vinyl-pyridine are decomposed almost completely by heating with strong phosphoric acid-iodic acid at the temperature over 253° or 260°C, but at the same time oxygen is liberated by the self-decomposition of iodic acid. On the other hand, it was also found that amine, ammonium salt, and nitrile are completely decomposed at the temperature of 233°C, while pyridine compounds are not attacked at all at the same temperature. From these results it may be suggested that nitrogen in amines, ammonium salts, etc. and nitrogen in pyridine compounds would be separately determined by controlling the decomposition temperature with strong phosphoric acid-iodic acid, if oxygen liberated from iodic acid could be removed by any suitable means in the case of analysis of pyridine compounds.

Full details will be reported elsewhere in the near future.

Mitsubishi Rayon Co., Ltd.
Kyobashi, Tokyo

Cyclopolysiloxanes from Cohydrolysis of Dimethyldichlorosilane with Methyldichlorosilane and Ethyldichlorosilane

By Rokuro ŌKAWARA, Ukiko TAKAHASHI and Minoru SAKIYAMA

(Received March 4, 1957)

Recently, a series of linear and branched methylhydropolysiloxanes having the formula $\mathbf{M'D'_nM'}$[a] (n=0–6), **MM'**, **M'DM'**, **M'D'DM'**, $\mathbf{M'D_2M'}$, $\mathbf{M'_3}$, **T** and $\mathbf{MD'_nM}$ (n=1–6) have been reported[1,2]

Now we wish to report on the preparation and properties of methylhydrocyclotetrasiloxanes; $\mathbf{D_3D'}$, $\mathbf{D_2D'_2}$ and $\mathbf{DD'_3}$, and the similar ethylmethylhydrocyclotetrasiloxanes; $\mathbf{D_3D^*}$[b], $\mathbf{D_2D^*_2}$ and $\mathbf{DD^*_3}$. These compounds were obtained from the cohydrolysis of the mixture of methyldichlorosilane(III') (or ethyldichlorosilane (III*)) and dimethyldichlorosilane(II) in various mole ratios.

Since it has been known that the hydrolysis in an acidic medium is favourable to the formation of the lower membered rings[3] and further, the amount of Si-H split by hydrolysis is not so large even in the case of direct hydrolysis[1], the hydrolysis was carried out by adding chlorosilanes to the mixture of ether and water. Then the product was distilled and thermally rearranged under reduced pressure (10–20 mm.). Almost all the hydrolyzate distilled out as an untreated hydrolyzate and the remaining gel was also thermally rearranged completely without any residue up to the still-pot temperature of 450°C. The amount of the untreated and thermally rearranged hydrolyzates varied with the composition of the starting mixture, but their active hydrogen contents are nearly the same as is shown in Table I. Then both the hydrolyzates were united and the composition of the tetrasiloxanes was determined by fractionation through a high efficient column. About 40–50% of the hydrolyzate was found to be the tetrasiloxanes. For example, the distribution of the tetrasiloxanes $\mathbf{D_nD^*_{4-n}}$ (n=0–4), is shown in Fig. 2 with regard to the composition of the starting mixture.

Formally, $\mathbf{DD'_3}$, $\mathbf{D_2D'_2}$ and $\mathbf{D_3D'}$ are obtained by substituting one unit of **D'** in tetramethylcyclotetrasiloxane successively by **D** unit. Among them, $\mathbf{D_2D'_2}$ would consist of at least two isomers: $\overline{\text{-DDD'D'-}}$ and $\overline{\text{-DD'DD'-}}$. Sauer[4] has already characterized methylhydrocyclopolysiloxanes $\mathbf{D'_n}$ (n=4–6), but for comparison, $\mathbf{D'_n}$ (n=4–7) was also prepared and characterized in this paper.

Regular changes of the physical constants are read from Table II, referring to the compounds of $\mathbf{D_nD'_{4-n}}$ and $\mathbf{D_nD^*_{4-n}}$ (n=0–3). For comparison, the effect of substituting one **D'** unit successively by **D** unit in $\mathbf{D'_4}$ and $\mathbf{M'D'_2M'}$[c] is summarized in Table III. It may be seen that the effect of substituting one **D'** unit by one **D** unit is the same as the substitution of H(-Si) by one methyl group. In the linear compounds, the effect of introduction of the second methyl group does not cause such a marked increase of refractive index as that of the first methyl group but the density increases by nearly the same amount. However in the series of cyclocompounds $\mathbf{D_nD'_{4-n}}$, successive substitution of a methyl group causes the regular increase of boiling point and refractive index and the regular decrease of density.

Referring to the series of isomeric compounds $\mathbf{D_nD^*_{4-n}}$ (n=0–4), the gradual increase of boiling point, Δd_1^{20}, and Δn_1^{20} are pointed out by substituting **D** unit successively by **D*** unit. Thus the boiling point, the refractive index and the density of $\mathbf{D^*_4}$ assumed by this relation were not in accordance with that of the tetramer, but accorded well with the trimer reported

1) R. Ōkawara and M. Sakiyama, This Bulletin, **29**, 236 (1956).
2) R. Ōkawara and M. Sakiyama, ibid., **29**, 547 (1956).
a) The shorthand notations were indicated in the preceding papers 1) and 2).
b) In this paper, in addition to the previous notation, **D*** will be used to indicate C_2H_5SiHO unit.
3) W. I. Patnode and D. F. Wilcock, *J. Am. Chem. Soc.*, **68**, 358 (1946).
4) R. O. Sauer, S. D. Brewer and W. I. Scheiber, ibid., **68**, 962 (1946).
c) Refractive index and density of the linear tetramers $\mathbf{M'D'_2M'}$, **M'D'DM'** and $\mathbf{M'D_2M'}$ have been reported (*loc. cit.* 1) and 2)) n_1^{20}: 1.3830, 1.3862 and 1.3875, d_4^{20}: 0.8613, 0.8623 and 0.8632, respectively.

in the previous paper[5] in which they were assigned by the determination of the molecular weight in dioxane. Here, again, the first four members of D^*_n were isolated from the hydrolyzate of ethyl dichlorosilane(III*). From the molecular weight determination in benzene and in dioxane, and further from the wave length of the infra-red absorption band associated with the Si-O stretching vibration, the first member of D^*_n, though small in amount and unstable, was assigned to be cyclotrimer and the erroneous assignment in the previous paper has been corrected.

Experimental

Starting Materials. — Dimethyldichlorosilane (II) and methyldichlorosilane(III') used in these experiments were supplied from the Shin-etsu Chem. Ind. Co. Ethyldichlorosilane(III*) was prepared by the reaction of industrial ethylchloride with silicon-copper. The two isomeric chlorosilanes, II and III* have been reported to have a close boiling point 70.2°C[6] and 74.9°C[7], respectively. For fear of contamination of a small amount of II, which would be formed in the course of the direct synthesis, the fractions of III* were carefully fractionated by a Stedman column of about 30 theoretical plates. The constant boiling plateau (74°–75°C) having the constant chlorine content was used for the preparation, and especially for the preparation of D^*_n the back part of the plateau was taken to avoid the contamination of II.

Anal. Found: Cl, 54.8 %. Calcd. for $C_2H_6SiCl_2$ Cl, 54.9 %.

Fractionation of the Polysiloxanes. — Throughout this experiment, the hydrolyzates were fractionated through a Stedman column of about 50 theoretical plates.

Analysis of Active Hydrogen. — Active hydrogen content % H(-Si), was measured by decomposing the sample with butanolic sodium hydroxide in a Zerewitinoff's apparatus.

Hydrolyzates from the Acidic Medium. — The mixture of chlorosilanes was added to the ice-cooled mixture of ether and water with vigorous stirring. The organic layer was washed with water until it became neutral to methylorange. The oily product from the ether layer was distilled under reduced pressure at 10–20 mm., and the untreated and thermally rearranged products were collected separately in an ice-cooled receiver. The results with regard to the chlorosilane mixture of II and III* are given in Table I.

The untreated and thermally rearranged products which distilled out up to 300°C and 450°C respectively, were collected together and rigorously fractionated. For example, the result of Expt. 2 is shown in Fig. 1.

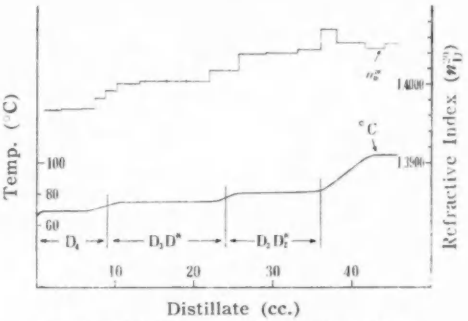

Fig. 1. Distillation curve of the cohydrolyzate (Expt. 2 of Table 1) at 18 mm.

In Fig. 1, the complete plateaus of D_4, D_3D^* $D_2D^*_2$ were found and it was easy to calculate the percentage composition of them by cutting on the distillation curve. The plateau of DD^*_3 was not found, but from the refractive index, which was higher than the neighboring fractions at the next portion of $D_2D^*_2$, it was supposed to be present in this portion, although small in amount. The distribution of the tetrasiloxanes thus determined is shown in Fig. 2.

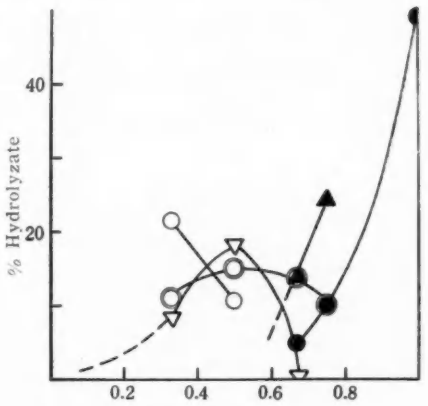

Fig. 2. Distribution of tetrasiloxanes $D_nD^*_{4-n}$ ($n=0-4$) with regard to the mole fraction of ethyldichlorosilane (III*/II+III*).

Fractionation of the hydrolyzate of III* (Expt. 5 of Table I) gave the first plateau at 67°C/20 mm., which amounted to 9 % of the hydrolyzate. The succeeding plateaus amounting to 48, 25 and 6 % of the hydrolyzate, were found to be those of

5) R. Ōkawara, E. Asada and T. Watase, This Bulletin, **26**, 141 (1953).
6) W. F. Gilliam, E. M. Hadsell, H. A. Liebhafsky and M. M. Sprung, *J. Am. Chem. Soc.*, **73**, 4252 (1951).
7) R. N. Meals, ibid., **68**, 1880 (1946).

TABLE I

COHYDROLYZATES FROM THE MIXTURE OF DIMETHYLDICHLOROSILANE(II) AND ETHYLDICHLOROSILANE(III*)

In each experiment, the mixture of the starting materials was added to the hydrolyzing medium which consisted of 500 cc. of ether and 1 l. of water.

Expt. No.	Starting Materials	mol.	Hydrolyzate Total (T) % theory	Hydrolyzate Untreated % T	%H(−Si) Untreated	%H(−Si) Thermally Rearranged (Calcd.)
1	III*	0.5	84	82	—	—
	II	1.0			(0.45)	
2	III*	0.76	80	73	—	0.67
	II	0.76			(0.68)	
3	III*	1.0	83	63	0.90	0.80
	II	0.5			(0.90)	
4	III*	1.2	83	71	1.00	0.94
	II	0.4			(0.98)	
5	III*	0.83	84	50	1.35	1.32
					(1.35)	

TABLE II

CYCLIC POLYSILOXANES

Compound[a]	Boiling point °C/mm.	Refractive index n_D^{20}	Density d_D^0	Molar refraction Found (Calcd.)[c]	Molecular weight Found[d] (Calcd.)	% H(-Si) Found (Calcd.)
$\mathbf{D'}_4$	133/760 ((134.5))[b]	1.3870 ((1.3870))	0.9913 ((0.9912))	57.22 (57.08)	— (240.5)	1.67 (1.68)
$\mathbf{D'}_3\mathbf{D}$	143/760	1.3900	0.9809	61.51 (61.45)	— (254.6)	1.19 (1.19)
$\mathbf{D'}_2\mathbf{D}_2$	154/760	1.3927	0.9709	65.96 (65.82)	— (268.6)	0.75 (0.75)
$\mathbf{D'D}_3$	165/760	1.3950	0.9620	70.55 (70.19)	— (282.6)	0.35 (0.36)
$\mathbf{D'}_5$	60/14 ((168.7))	1.3918 ((1.3912))	0.9986 ((0.9985))	71.66 (71.35)	— (300.7)	1.67 (1.68)
$\mathbf{D'}_6$	83/14 ((92.8/21))	1.3943 ((1.3944))	1.003 ((1.006))	86.10 (85.62)	359 (360.8)	1.66 (1.68)
$\mathbf{D'}_7$	102/14	1.3958	—	—	411 (420.9)	1.65 (1.68)
$\mathbf{D^*}_3$	67/20	1.4078	0.9673	56.71 (56.70)	218 (222.5)	1.38 (1.36)
$\mathbf{D^*D}_3$	180/760, 75/18	1.4003	0.9598	74.97 (74.82)	— (296.6)	0.34 (0.34)
$\mathbf{D^*}_3\mathbf{D}_2$	188/760, 82/19	1.4042	0.9658	75.14 (75.08)	292 (296.6)	0.67 (0.68)
$\mathbf{D^*}_3\mathbf{D}$	201/760, 88/16	1.4090	0.9727	75.39 (75.34)	— (296.6)	1.01 (1.02)
$\mathbf{D^*}_4$	208/760, 105/20 ((106/20))	1.4141 ((1.4138))	0.9808 ((0.9836))	75.39 (75.60)	294[e] (296.6)	1.36 (1.36)
$\mathbf{D^*}_5$	80/2 ((135/20))	1.4187 ((1.4176))	0.9899 ((0.9920))	94.53 (94.50)	— (370.8)	1.37 (1.36)
$\mathbf{D^*}_6$	101/2 ((165/20))	1.4215 ((1.4200))	0.9942 ((1.0023))	113.6 (113.4)	— (445.0)	1.35 (1.36)

a) $\mathbf{D'}=CH_3SiHO$, $\mathbf{D}=(CH_3)_2SiO$, $\mathbf{D^*}=C_2H_5SiHO$.

b) Reported values are indicated in brackets, (( )). The data of $\mathbf{D'}_n$ and $\mathbf{D^*}_n$ are those reported in 4) and 5) (*loc. cit.*), respectively, but for $\mathbf{D^*}_n$, only the polymer size has been corrected.

c) Calculated from bond refractivities by E. L. Warrick, *J. Am. Chem. Soc.*, **68**, 2455 (1946).

d) Cryoscopic measurements in benzene.

e) The values of 293 and 295 were obtained at the concentration of 1.1 g. and 2.3 g. per 100 g. of benzene. Also, from the depression of 0.220° and 0.421°C at the concentration of 1.32 g. and 2.54 g. of the sample in 100g. of dioxane (b. p. 101°C, m. p. 11.67°C, molecular depression 4.95) the molecular weight 298 and 299 were obtained.

succeeding polymers as shown in Table II. The following small plateau at 120°C/2 mm. was also found, but it was too small in amount to be characterized accurately.

Tetrasiloxanes $\mathbf{D}_n\mathbf{D}'_{4-n}$ ($n=0-3$) were prepared as above from the hydrolyzate (yield: 83–87% theory) of the mixture of II and III′ in various molar ratios. In the case of smaller molar ratios, x' (III′/II), the gel formed above 300°C was completely pyrolyzed until 400°C, but with increasing molar ratios, almost all the hydrolyzate came out below 300°C without any perceptible gelation in a still-pot. In tetrasiloxanes, the elevation of the boilng point at 760 mm. was found to be about 10°C when one unit of **D′** is substituted by one unit of **D**, but it required repeated distillation to obtain satisfactorily pure compounds.

To obtain a series of polymers $\mathbf{D}'_n$, the hydrolyzate(Found: H(-Si), 1.65%. Calcd. for$(CH_3SiHO)_n$: H(-Si), 1.67%) of III′, which distilled out below 300°C at 10–20 mm., was fractionated. A complete plateau was not found at the boiling point of the cyclotrimer (Reported[8]: b. p. 93.7°C) but a knick point. The succeeding plateau amounting to 40, 23, 8, 4 and 3% of the hydrolyzate, were found to be those of $\mathbf{D}'_4$ to $\mathbf{D}'_8$. Since the plateau of $\mathbf{D}'_8$ gradually rose from 114° to 118°C at 15 mm., and its active hydrogen content was somewhat lower (Found: H(-Si), 1.63%), polymers until $\mathbf{D}'_7$ are shown in Table II. The active hydrogen content of those polymers decreased slowly and regularly with increasing polymer size. The H(-Si) of the residue was 1.48%, from which it may be enough to suppose the contamination of compounds other than $\mathbf{D}'_n$.

TABLE III

CHANGES OF PHYSICAL CONSTANTS DUE TO SUCCESSIVE SUBSTITUTION OF **D′** BY **D** UNIT IN TETRASILOXANES

Compound	Numbers of **D** unit substituted	Boiling point at 760 mm. Δ°C	Increase of Refractive index $\Delta n_D^{20}\times10^4$	Density $\Delta d_4^{20}\times10^3$
$\mathbf{M'D'_2M'}$	1	—	32	1
	2	—	13	1
$\mathbf{D'_4}$	1	10	30	−10
	2	11	27	−10
	3	11	23	− 9
	4[d]	10	18	− 6

Infra-red Spectra of $\mathbf{D}^*_n$.—The contamination of **D** unit in $\mathbf{D}^*_n$ can easily be detected by determining the active hydrogen content and also by the apearance of a sharp band in the infra-red spectra near 1260 cm^{-1}, which has been attributed to the methyl grouping in CH_3-(Si). In this experiment, the absorption spectra were obtained with a Hilger H-800 infra-red spectrophotometer with a rock salt prism. Samples were observed as solution, 3% in carbon disulfide being used in the range of 650–1300 cm^{-1}.

In the region 1200–1300 cm^{-1} two bands were found in the figure of $\mathbf{D}_n\mathbf{D}^*_{4-n}$ ($n=1-3$): the one near 1260 and the other near 1240 cm^{-1}, which can be attributable to CH_3CH_2-(Si) group[9]. But the figure of $\mathbf{D}^*_n$ showed only the latter band. The band associated with the stretching of Si-O bond was found at 1023, 1085, 1089 and 1086 cm^{-1} for the first four members of $\mathbf{D}^*_n$, respectively. Since the cyclic trisiloxanes[9] have been reported to have the characteristic absorption band at 1010–1020 cm^{-1} and the higher cyclic polysiloxanes near 1080–1090 and 1050–1080 cm^{-1} respectively, it may be natural to suppose that the first member of $\mathbf{D}^*_n$ obtained in this experiment is cyclic trimer. The result accorded well with the molecular weight determination in benzene as shown in Table II.

The measurement of the physical properties of cyclotrimer $\mathbf{D}_3$* was carried out immediately after the fractionation and the infra-red spectra were measured after four days. During the measurement, only a slight change of refractive index was observed by the samples which were reserved in an ice box. All the samples which were sealed in glass ampoules became viscous fluid or gel in summer (room temperature of over 30°C) after three months, but there was found no perceptible increase of pressure in the ampoules. Infra-red spectra of the viscous fluid, after four months, gave rise to a strong band at 1094 cm^{-1} and the intensity of the band at 1023 cm^{-1}, characteristic to the cyclotrisiloxane ring, decreased. But the other compounds sealed in soft glass ampoules showed no change of refractive index.

Summary

1) Cyclotetrasiloxanes having **D′** and **D**, and **D*** and **D** units have been prepared and characterized.

2) Methylhydrocyclopolysiloxanes $\mathbf{D}'_n$ ($n=4-7$) and ethylhydrocyclopolysiloxanes $\mathbf{D}^*_n$ ($n=3-6$) have also been prepared and characterized. The erroneous assignment given to the latter compounds have been corrected.

3) Triethylcyclotrisiloxane $\mathbf{D}^*_3$, the first member of $\mathbf{D}^*_n$ was found to be an unstable compound.

Department of Applied Chemistry
Faculty of Engineering, Osaka
University, Miyakojima-ku,
Osaka

8) S. D. Brewer, ibid., **70**, 3962 (1948).

d) For $\mathbf{D}_4$, the reported values (*loc. cit.* 3)), n_D^{20} 1.3968 and d_4^{20} 0.9558 were used.

9) C. W. Young, P. C. Servais, C. C. Currie and M. J. Hunter, ibid., **70**, 3758 (1948).

Solvent Selectivity of Liquid Ammonia for Pure Hydrocarbons

Tie-Line Data and Comparison of Selectivity with Other Solvents

By Kiyoharu ISHIDA

(Received February 25, 1957)

Introduction

Results of extensive studies on the separation of petroleum fractions with liquid ammonia as a solvent, which include the fundamental solubility relationships for various hydrocarbon types and the tests on pilot plant extractions, have recently been published and the utility and the versatility of liquid ammonia as a solvent were stressed[1]. The fact that liquid ammonia has good solvency and selectivity for separating mixtures of naphthenic and aromatic hydrocarbons was clarified through the studies on the system of methylcyclohexane—toluene—liquid ammonia. It has also been demonstrated that it is important to control the dissolving power of the ammonia solvent so that the amount of hydrocarbon in the solvent phase lies between about 10 and 30 weight % either by temperature reduction or water injection or both, in order to prevent the decrease of selectivity accompanied by the increase of solubility. However, from the viewpoint of phase equilibrium, apart what has just been stated above and the relative distribution ratio at 10% solubility, few fundamental equilibrium data are given.

In order to determine the solvency and selectivity of liquid ammonia as a solvent for separating more soluble hydrocarbons such as aromatics and low molecular weight hydrocarbons, systems of cyclohexane—benzene, *n*-hexane—benzene, and ethylbenzene—styrene, the last as an example of two aromatic hydrocarbons, whose separation is a practical problem, were selected, and equilibria of ternary systems of these two components and liquid ammonia were measured. Furthermore, the comparison of selectivity of liquid ammonia with other solvents, which are used or are usable for the separation of various hydrocarbons, was attempted.

1) M. R. Fenske, R. H. McCormick, H. Lawroski and R. G. Geier, *A. I. Ch. E. Journal*, **1**, 335 (1955).

Experimental Procedure and Materials

The equilibrium data were determined in the same way as described in Part I of this series[2,3]; *n*-hexane and cyclohexane used in the present study are the same materials as described in Part II[3].

Commercial benzene was purified by the usual method and the fraction of b.p. 80.0–80.1°C, m.p. 5.53°C, d_4^{20} 0.8784, n_D^{20} 1.5011, was used.

Ethylbenzene was prepared from bromobenzene and ethyl bromide by the Fittig reaction and was fractionated to obtain one, having constants of b.p. 136.0°C, d_4^{20} 0.8670, n_D^{20} 1.4959.

Styrene was kindly supplied by Nippon Paint Co., Ltd. (purchased from Dow Chemical Co.), and showed $b.p._{24\cdot1}$ 48°C, d_4^{20} 0.9059, n_D^{20} 1.5468, and bromine number[4] of 151.2 (theoretical: 153.3).

The ternary system including styrene was prepared by the use of styrene freshly fractionated under reduced pressure, and after the determination of ammonia, the composition of the binary system of ethylbenzene and styrene was determined by measuring specific gravity, refractive index, and bromine number of the raffinate or the extract. For this system, no correction was made for the slight loss of hydrocarbons due to the volatilization during the determination of ammonia, because their vapor pressures at experimental temperatures are small and nearly of the same order.

Results

Equilibrium data for the system *n*-hexan-benzene-liquid ammonia (20°C) are shown in Table I, those for cyclohexane-benzene-liquid ammonia (20°C and 0°C) in Table II, and those for ethylbenzene-styrene-liquid ammonia (0°C and −15.5°C) in Table III. The data are presented graphically in Fig. 1–3. Both cyclohexane and benzene are present as crystals at 0°C, but their mixtures with liquid ammonia are liquids at 0°C lowering the melting point.

As will be clear from Fig. 1 and 2, aromatic hydrocarbons are selectively extracted from C_6-hydrocarbon mixtures,

2) K. Ishida, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **56**, 469 (1953).
3) Ibid., **57**, 479 (1954).
4) H. L. Johnson and R. A. Clark, *Anal. Chem.*, **19**, 869 (1947).

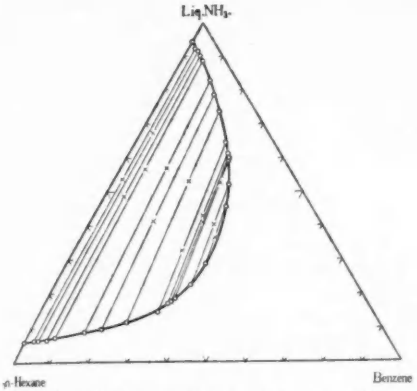

Fig. 1. System *n*-Hexane-Benzene-Liq. NH_3 at 20°C, wt. %.

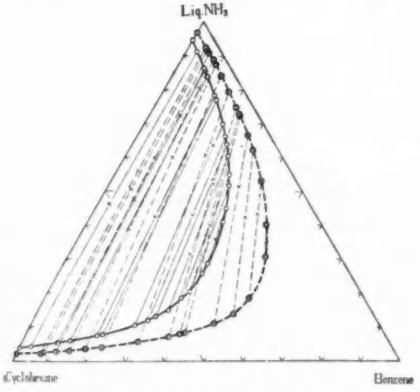

Fig. 2. System Cyclohexane-Benzene-Liq. NH_3 at 20°C and 0°C, wt. %.
—○— 20.0°C
– –◎– – 0.0°C

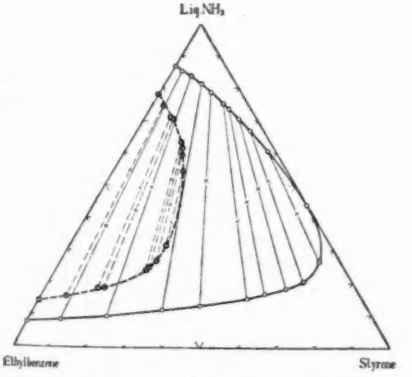

Fig. 3. System Ethylbenzene-Styrene-Liq.NH_3 at 0°C and −15.5°C, wt. %.
– –◎– – 0.0°C
—○— −15.5°C.

showing little difference between the paraffinic and naphthenic hydrocarbon present as a diluent. This is in accordance with the expectation from the equilibrium data for the system *n*-hexane-cyclohexane-liquid ammonia[3].

It seems that the separation of aromatic hydrocarbon mixture with the same number of carbon atoms, which contains another compound having more highly unsaturated properties, will be possible by the extraction using liquid ammonia as a solvent, since the increase of unsaturated properties increases the solubility for the solvent. Table III and Fig. 3 indicate that liquid ammonia is also usable for such separation, and that when the extraction is carried out at −15.5°C, the mixture of ethylbenzene and styrene can be separated into the raffinate containing 5 wt. % styrene and the extract containing 98 wt. % styrene under the condition of total reflux with minimum number of theoretical stages of 15.

The composition at plait point in Tables I–III (b) was estimated from Hand plot[5] according to Treybal, et al[6]. The slope of the straight line changes near the plait point for the systems cyclohexane-benzene-liquid ammonia and ethylbenzene-styrene-liquid ammonia at 0.0°C. The method of Othmer and Tobias[7] also gives the same results as by Hand plot. When the author's method[8] is used, in which the ratio of the concentration of the diluent in the diluent phase to the concentration of the solvent in the solvent phase against the former concentration is plotted on double logarithmic coordinates, the data in Table II give two straight lines of different slopes, but all other systems satisfy a linear relationship within the range of experimental error.

Comparison of Solvent Selectivity

There are various measures[1,9,10,11,12,13]:

5) D. B. Hand, *J. Phys. Chem.*, **34**, 1961 (1930).
6) R. E. Treybal, L. D. Weber and J. F. Daley, *Ind. Eng. Chem.*, **38**, 817 (1946).
7) D. F. Othmer and P. E. Tobias, ibid., **34**, 693 (1942).
8) K. Ishida, This Bulletin, **29**, 956 (1956).
9) K. W. Saunders, *Ind. Eng. Chem.*, **43**, 121 (1951).
10) D. A. Skinner, ibid., **47**, 222 (1955).
11) E. C. Medcalf, A. G. Hill and G. N. Vriens, *Petroleum Refiner*, **30**, No. 7, 97 (1951). He used the value at infinite dilution.
12) There are some investigators using the term "separation factor" in the same meaning as the relative distribution ratio, β. For example; B. Weaver, *Anal. Chem.*, **26**, 474 (1954). Usually, β is used for selectivity, e. g., L. F. Crooke, Jr., and M. Van Winkle, *Ind. Eng. Chem.*, **46**, 1474 (1954); A. E. Skrzec and N. F. Murphy, ibid., **46**, 2245 (1954), and so on. See also Ref. 14 and 22.
13) L. Alders, "Liquid-Liquid Extraction", Elsevier Pub. Company, London (1955), p. 85.

TABLE I

EQUILIBRIUM DATA FOR THE SYSTEM *n*-HEXANE-BENZENE-LIQUID AMMONIA AT 20.0°C, WT. %

Total Mixture		Hydrocarbon Layer		Solvent Layer	
Benzene Wt. % (Solvent-free Basis)	NH_3 Wt. %	NH_3 Wt. %	Benzene Wt. % (Solvent-free Basis)	NH_3 Wt. %	Benzene Wt. % (Solvent-free Basis)
0.0	—	6.1	—	94.4	—
4.7	53.9	6.5	2.7	92.5	24.6[a]
9.7	67.3	6.6	4.0	91.8	34.0
9.7	48.6	6.6	6.3	90.2	42.7
15.1	56.6	7.1	8.3	88.7	48.6
27.9	56.9	8.8	16.0	82.7	60.0
27.9	41.3	9.6	20.7	78.6	62.8
41.3	52.8	11.7	27.1	73.7	65.0
41.3	32.7	14.8	35.7	64.5	65.9
49.1	42.9	17.2	38.3	61.5	65.6
49.1	40.8	17.8	39.4	60.2	65.5
58.2	52.6	18.8	40.4	59.3	65.3
54.0	40.3	22.7	45.3	52.1	63.2
54.0	36.6	29.0	50.3	45.7	60.0
Plait Point[b]		39.7	56.7	39.7	56.7

a) This value was calculated from the concentrations of ammonia in both layers and the compositions of the total mixture and raffinate.

b) The plait point was estimated according to Treybal et al.[6]

for the comparison of selectivity, but the useful method for comparing the ability of solvents has not been established. It is inconvenient to compare the selectivity of various solvents from the available data by the relative distribution ratio[1,11,12] or the selective power[13], since they are not always constant in the entire separation zone for all ternary systems. Quantitatively, selectivity may be represented more satisfactorily by the selectivity diagram[14] which expresses the relation between y and x, where y is the concentration of the solute in the extract on a solvent-free basis and x is the corresponding concentration in the raffinate. For example, selectivity diagrams for the system cyclohexane-benzene-liquid ammonia at 20°C and 0°C are shown in Fig. 4, a and b, respectively.

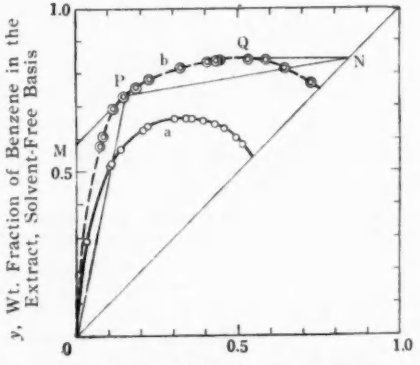

Fig. 4. Selectivity Diagrams for the System Cyclohexane-Benzene-Liq. NH_3, Ammonia as solvent.

If the selectivity I is defined as y-x, then I represents the degree of separation of the solute and the diluent, and is directly related to the selectivity diagram as shown in Fig. 4[15]. The maximum degree of separation of two components in one equilibrium stage is given by I_{max}. The greater the value of I_{max}, the more effective will be the separation. In addition, among solvents having an equal value of I_{max}, the greater the value of y_{max}, where y_{max} is the maximum concentration of the solute in the extract, the higher will be the purity of the solute obtained by the extraction using that solvent under the given condition. It would be most practical to cmpare the selectivity of solvents by taking account of I_{max} as well as y_{max} from the viewpoint of separation of the solute and the diluent. In Fig. 4, I_{max} on curve b is represented as MO and y_{max} as the value

14) R. E. Treybal, "Liquid Extraction", McGraw-Hill Book Company, Inc., New York (1951), p. 87.

TABLE II

EQUILIBRIUM DATA FOR THE SYSTEM CYCLOHEXANE—BENZENE—LIQUID AMMONIA AT 20.0°C AND 0.0°C, WT. %

Total Mixture		Hydrocarbon Layer		Solvent Layer	
Benzene Wt. % (Solvent-free Basis)	NH_3 Wt. %	NH_3 Wt. %	Benzene Wt. % (Solvent-free Basis)	NH_3 Wt. %	Benzene Wt. % (Solvent-free Basis)
At 20°C					
0.0	—	4.0	—	94.2	—
5.2	46.2	4.4	3.3	91.4	29.0
16.2	47.8	5.7	10.4	86.2	52.0
28.4	72.3	5.5	10.8	85.7	52.4
44.9	80.1	6.1	13.9	84.0	57.0
28.4	42.3	7.7	20.6	78.2	62.8
44.9	65.4	7.9	22.1	77.1	64.0
56.7	63.4	10.6	30.4	70.0	66.3
44.9	43.2	12.0	33.9	66.0	66.3
54.9	53.6	12.8	35.9	63.8	66.2
44.9	31.6	14.9	39.4	60.1	65.6
52.5	40.1	18.3	43.0	54.8	64.4
52.5	36.9	20.3	45.7	51.4	63.2
54.4	35.8	25.4	49.3	44.9	60.4
56.7	38.7	28.4	51.3	40.8	58.4
Plait Point[b]		34.4	54.8	34.4	54.8
At 0.0°C					
0.0	—	2.1	—	96.8	—
12.4	56.0	2.6	7.2	92.5	58.0
12.4	50.7	2.7	8.2	91.8	60.8
19.0	59.5	2.8	11.3	91.1	69.3
19.0	38.8	3.2	14.7	88.9	73.2
30.4	60.1	3.7	18.4	87.4	75.8
30.4	42.7	4.1	22.9	84.2	78.2
51.0	60.5	5.7	32.3	79.4	81.8
55.1	52.3	7.1	40.5	74.7	83.6
51.0	37.2	7.9	43.5	72.9	83.8
55.1	43.2	8.3	44.8	72.2	84.0
68.4	51.4	10.8	53.1	66.7	84.1
68.4	42.5	13.5	58.9	62.2	84.0
74.1	43.6	18.3	64.3	53.1	81.3
74.1	34.8	30.4	72.8	40.0	77.1
Plait Point[b]		35.5	75.2	35.5	75.2

b) Cf. Table I.

on the ordinate of Q point, and then $I_{max} \cdot y_{max}$ would be twice the area of the triangle PON. Therefore, if the maximum separation factor is defined by the value of $I_{max} \cdot y_{max}$, it will be indicated by the definite value of $I_{max} \cdot y_{max}$ between 1.0 in the most ideal case, and zero with no effectiveness for the separation. This will be used as the convenient measure of comparison for selectivity.

Values of $I_{max} \cdot y_{max}$ calculated from the available data of ternary systems with liquid ammonia as one component are given in Table IV. In order to compare with other solvents, the values of $I_{max} \cdot y_{max}$ of representative solvents, which have been used or may be used as a solvent for the separation of hydrocarbons, are listed in the order of magnitude.

There are many factors other than selectivity which must be considered in choosing a solvent for a liquid extraction process, and it is evident that solvent power is the most important factor among them. In general, the amount of solvent in the raffinate phase is small and the large amount of solvent for recovery is carried in the solvent phase. If the diluent and the solute are to be separated as far as possible, a major amount of

TABLE III

EQUILIBRIUM DATA FOR THE SYSTEM ETHYLBENZENE STYRENE LIQUID AMMONIA AT 0.0°C AND −15.5°C, WT. %

Total Mixture		Hydrocarbon Layer		Solvent Layer	
Styrene Wt. % (Solvent-free Basis)	NH_3 Wt. %	NH_3 Wt. %	Styrene Wt. % (Solvent-free Basis)	NH_3 Wt. %	Styrene Wt. % (Solvent-free Basis)
At 0.0°C					
0.0	—	14.1	—	78.1	—
9.1	54.8	15.7	8.1	74.7	11.7
19.0	49.0	18.3	17.3	71.1	23.0
20.7	42.3	18.4	19.2	70.5	26.2
34.4	51.9	24.0	31.5	63.4	36.9
34.9	46.8	24.8	32.5	61.7	38.2
36.1	44.0	27.0	34.5	59.5	38.5
38.0	38.9	31.5	37.2	54.3	40.2
Plait Point[b]		47.0	41.2	47.0	41.2
At −15.5°C					
0.0	—	8.0	—	87.0	—
10.5	37.3	8.5	9.9	85.2	16.5
25.0	49.4	9.6	23.0	83.9	34.3
40.6	43.8	11.4	39.0	81.4	51.5
53.3	51.4	12.7	50.2	78.8	62.4
66.3	39.0	15.1	64.8	75.1	73.7
72.0	45.1	16.6	70.2	73.6	78.0
79.8	49.0	18.2	77.4	70.3	84.0
86.4	51.2	20.3	84.2	66.8	89.3
93.2	41.3	26.5	92.8	60.4	94.9
100.0	—	43.9[c]	—	43.9[c]	—

b) Cf. Table I.

c) Since −15.5°C is the upper critical solution temperature for the binary mixtures of styrene and liquid ammonia, the concentration of ammonia was estimated from the composition at the critical point.

solvent should be recovered at the end of the enriching section of the extraction tower where the extract is obtained. Therefore, the amount of other components dissolved in that solvent, $(1-Sy_{max})$, where Sy_{max} is the concentration of the solvent in the solvent phase at y_{max}, will be an index of solvent power of that solvent. This value is given in the column 8 and the product of that value and $I_{max} \cdot y_{max}$ is given in column 9 in Table IV, as a comprehensive index.

As will be clear from Table IV, liquid ammonia is a poor solvent for the separation of paraffins and naphthenes[3,26], but for the separation of C_6–C_7 saturated hydrocarbons and aromatics or olefins, it is comparable to diethyleneglycol, better than liquid sulfur dioxide with respect to the selectivity and the solvent power. As ammonia has relatively high vapor pressure, it is comparatively easy to separate liquid ammonia from other components. And also, its extensive use as a mixed solvent is possible because of miscibility with water, lower alcohols, amines, and esters[1,27]. Considering the close relationship between the production of ammonia and the petrochemical industry, it is thought that there is a possibility of the use of liquid ammonia as a solvent for the separation of hydrocarbons.

Summary

Equilibria for the systems *n*-hexane-benzene-liquid ammonia (20°C), cyclohexane-benzene-liquid ammonia (20°C and 0°C), and ethylbenzene-styrene-liquid ammonia (0°C and −15.5°C) were determined. It was shown that the ability of a solvent would be most practically compared by the product of the maximum

26) A. W. Francis, ibid., **36**, 764 (1944).

27) U. S. Pat. 2,721,164 (Oct. 18, 1955), *C. A.*, **50**, 2968c (1956); U. S. Pat. 2,723,940 (Nov. 15, 1955), *C. A.*, **50**, 3748d (1956).

TABLE IV

SELECTIVITIES AND CAPACITIES OF SOLVENTS FROM VARIOUS SYSTEMS

Components			Temp. °C	I_{max} Wt. Fraction	y_{max} Wt. Fraction	$I_{max} \cdot y_{max} \times 10^2$	$1\text{-}Sy_{max}$ Wt. Fraction	$I_{max} \cdot y_{max} \times (1 - Sy_{max}) \times 10^2$	Ref.
Diluent	Solute	Solvent							
n-Hexane	Methylcyclopentane	Aniline	34.5	0.115	1.00	11.5	0.515	5.9	16
〃	Cyclohexane	Liq. NH_3	20	0.055	1.00	5.5	0.058	0.3	3
n-Heptane	〃	Furfural	30	0.135	1.00	13.5	0.139	1.9	17
〃	〃	Aniline	25	0.097	1.00	9.7	0.262	2.5	18
n-Hexane	Benzene	Ethylenediamine	20	0.615	0.848	52.1	0.225	11.7	19
〃	〃	SO_2	−28.9	0.61	0.68	41.5	0.15	6.2	20
〃	〃	Liq. NH_3	20	0.443	0.659	29.2	0.355	10.4	
Cyclohexane	〃	β,β'-Thiodipropionitrile	Room temp.	0.765	0.96	73.1	0.30	21.9	9
〃	〃	Liq. NH_3	0	0.585	0.842	49.3	0.333	16.4	
〃	〃	〃	20	0.433	0.664	28.8	0.300	8.6	
〃	〃	Nitromethane	25	0.375	0.588	22.1	0.29	6.4	21
n-Heptane	〃	Diethyleneglycol	25	0.686	1.00	68.6	0.313	21.5	22
〃	〃	92%-Diethyleneglycol-8% H_2O	125	0.56	1.00	56.0	0.285	16.0	22
〃	〃	SO_2	−28.9	0.63	0.73	46.0	0.16	7.3	20
〃	〃	Furfural	Room temp.	0.38	0.592	22.5	0.335	7.5	9
Methylcyclohexane	Toluene	Liq. NH_3	21.1	0.38	0.73	27.75	0.35	9.7	1
n-Heptane	〃	β,β'-Thiodipropionitrile	25	0.715	1.00	71.5	0.296	21.2	10
〃	〃	Liq. NH_3	−7.5	0.595	1.00	59.5	0.575	34.2	8
〃	〃	〃	0	0.668	0.955	64.8	0.418	27.1	2,8
〃	〃	〃	−15	0.556	1.00	55.6	0.268	14.9	8
〃	〃	Diethyleneglycol	25	0.490	1.00	49.0	0.17	8.3	10
〃	〃	SO_2	−28.9	0.66	0.73	48.2	0.14	6.8	20
〃	〃	Liq. NH_3	20	0.468	0.808	37.8	0.306	11.6	2,8
〃	〃	Aniline	25	0.290	0.470	13.6	0.266	3.6	13
〃	〃	97%-Acetic acid-3% H_2O	23	0.19	0.55	10.5	0.69	7.2	23
n-Heptane	Octene-1	Liq. NH_3	20	0.115	1.00	11.5	0.063	0.7	3
〃	〃	〃	0	0.108	1.00	10.8	0.032	0.3	3
Decalin	Tetralin	〃	20	0.415	1.00	41.5	0.136	5.6	24
〃	〃	〃	0	0.323	1.00	32.3	0.063	2.0	24
Ethylbenzene	Styrene	〃	−15.5	0.126	1.00	12.6	0.561	7.1	
〃	〃	Diethyleneglycol	25	0.103	1.00	10.3	0.271	2.8	25
〃	〃	Liq. NH_3	0	0.068	0.412	2.8	0.51	1.4	

15) K. Ishida, *Science Repts. Research Inst. Tohoku Univ.*, Ser. A, **5**, 377 (1953).
16) B. DeB. Darwent and C. A. Winkler, *J. Phys. Chem.*, **47**, 442 (1943).
17) E. N. Pennington and S. J. Marwil, *Ind. Eng. Chem.*, **45**, 1371 (1953).
18) T. G. Hunter and T. Brown, ibid., **39**, 1343 (1947).
19) A. P. C. Cumming and F. Morton, *J. Appl. Chem.*, **3**, 358 (1953).
20) C. N. Satterfield, J. H. Powell, Jr., E. A. Oster, Jr., and J. P. Noyes, *Ind. Eng. Chem.*, **47**, 1458 (1955).
21) H. I. Weck and H. Hunt, ibid., **46**, 2521 (1954).
22) G. C. Johnson and A. W. Francis, ibid., **46**, 1662 (1954).
23) D. F. Othmer and P. E. Tobias, ibid., **34**, 690 (1942).
24) K. Ishida, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **60**, 864 (1957).
25) M. G. Boobar, P. M. Kerschner, R. T. Struck, S. A. Herbert, N. L. Gruver and C. R. Kinney, *Ind. Eng. Chem.*, **43**, 2922 (1951).

value of selectivity and the maximum concentration of the solute in the extract, i. e. maximum separation factor. Selectivity and solvent power of some solvents were compared by this definition and it was recognized that liquid ammonia is comparable to diethyleneglycol as a solvent for the separation of saturated hydrocarbons and aromatic or olefinic hydrocarbons, rather than liquid sulfur dioxide.

The author wishes to record his thanks to Professor Tokura and his coworkers in this Laboratory for a gift of styrene.

The Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, Sendai

Organic Semiconductors with High Conductivity II. Structural Aspect of Violanthrene-Iodine Complex

By Hideo AKAMATU, Yoshio MATSUNAGA and Haruo KURODA

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Introduction

In the preceding paper[1], we have presented that polycyclic aromatic hydrocarbons form solid molecular complexes with bromine or iodine, and these complexes behave as typical semiconductors with high conductivity of 10^{0}–10^{-3} ohm^{-1}. cm^{-1} at room temperature and low activation energy for conduction, the energy gap of 0.1–0.2 eV. It has been suggested that the high conductivity is due to an appropriate electronic structure which arises from the formation of the molecular additive compounds. To throw light upon the mechanism of the electrical conduction in these organic materials, it should be most interesting to make clear the structure of these molecular complexes. In the present paper, the structural aspect of the violanthrene-iodine system is presented.

Violanthrene-iodine complex is the most stable among the complexes between polycyclic aromatic hydrocarbons and halogens so far as is known. The electrical resistivity varies as the composition varies, and has the minimum value at the composition in which the mole ratio of iodine to violanthrene (V) is 2, where the resistivity at room temperature is about 40 ohm. cm with the thermal energy gap of 0.15 eV.

The magnetic susceptibility-composition curve[2] shows a great discrepancy from the additive law, and has also the minimum value (depression of diamagnetism) at the same composition, where the discrepancy exceeds 35 per cent. Both these facts suggest the existence of molecular complex consisting of one molecule of violanthrene and two of iodine. On the other hand, a preliminary examination by X-ray revealed an amorphous pattern, while most of the other complexes showed sharp crystalline patterns.

In this paper, the thermodynamical study on the equilibrium of violanthrene-iodine system as well as the full examinations by X-ray are presented.

Preparation of the Complex and Isotherm of Violanthrene-Iodine System

The preparation of the complexes has been described in the previous papers. In the present case, however, with the purpose of studying the isothermal equilibrium between violanthrene and iodine, the following method was applied to the preparation of complexes having varied compositions. The crystalline powder of violanthrene of known quantity was treated with carbon tetrachloride solution of iodine for more than three days. After the equilibrium has been reached, the precipitated complex was filtered through glass wool and the concentration of iodine in the filtrate was determined by titration with 0.025 N aqueous solution of sodium thiosulfate. The composition of the complex obtained was estimated from the difference in concentration of iodine between the initial and the final solution.

Two isotherms have been obtained; one is at the room temperature 27 ± 1°C, and the other is at the temperature of refrigerated chamber -3 ± 2°C. The relation between the equilibrium

1) H. Akamatu, H. Inokuchi and Y. Matsunaga, This Bulletin, **29**, 213 (1956).
2) Y. Matsunaga, ibid., **28**, 475 (1955).

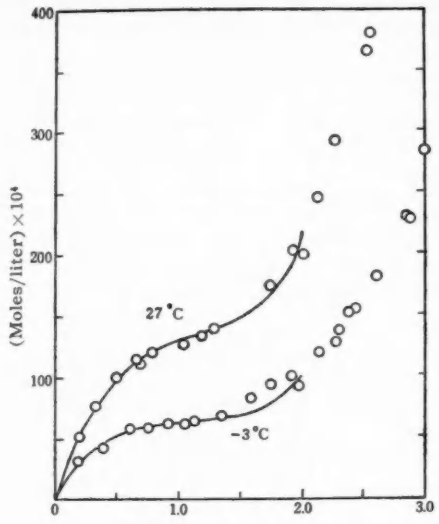

Fig. 1. Equilibrium concentration of iodine in carbon tetrachloride solution plotted against composition of the complex.

concentration of iodine in the carbon tetrachloride solution and in the complex is shown in Fig. 1.

Equilibrium in Violanthrene-Iodine System

Fig. 1 suggests that the observed isotherms are the ones near a boundary of the univariant and bivariant phases and just above the critical temperature, below which two solid phases should be separated, one has the ideal composition of $V \cdot 2I_2$ and the other is V.

Such an isotherm has been discussed by a few authors. Anderson[3] discussed the conditions of equilibrium of non-stoichiometric chemical compounds. Rees[4] derived the pressure-temperature-composition relations for two-component interstitial solid solutions. His theory is applicable to any non-stoichiometric system in which one component is volatile. Both theories are applicable to the present case. However, referring the results of density measurements described in the later section, Rees' model is more conveniently applicable to our case.

The problem is to derive the pressure-temperature-composition relation in a system composed of molecules A(violanthrene) and B (iodine) up to composition A_mB_n where m and n are small integers, and so delineate a boundary of the univariant and the bivariant phase. The fundamental assumptions are as follows.

The solvent lattice of A molecules is referred to as the parent lattice, and the solute component B is in equilibrium with molecules of B in the vapor phase. B molecules occupy interstitial sites in the parent structure*. Several kinds of site are assumed; they are distinguished from each other by the difference in the amount of energy which is gained by a B molecule against free molecular state when it occupies one kind of site. These energies are denoted as E^a, E^b *etc.* for the *a*th, *b*th *etc.* kind of site, respectively.

The interaction energies per pairs of B molecules in each kind of site are considered, and denoted as E^{aa}, E^{bb} *etc.* Furthermore, it is assumed that the number of the sites of the ith kind accessible for occupation by B molecule depends on the number of sites of the $(i-1)$th kind already occupied by B molecules. Let N stand for the total number of sites of the *a*th kind, N^a, N^b, N^c *etc.* for the numbers of sites of the *a*th, *b*th, *c*th *etc.* kinds occupied at equilibrium, and α, β *etc.* for the number of sites of the *b*th, *c*th *etc.* kind created for one of the *a*th, *b*th *etc.* kind occupied by a B molecule respectively. The contribution of the parent lattice of A molecules to the total partition function of the crystal is assumed to be independent of the contents of B molecules, so that it is concerned only with the factor representing the contribution of the added B molecules; then the extra configurational grand partition function is expressed as,

$$\begin{aligned}\Theta(T,\ \lambda^a,\ \lambda^b\cdots\cdots N^a,\ N^b\cdots\cdots) &= \sum_a\sum_b\cdots\cdots[\lambda^a\kappa^a(T)]^{N^a}[\lambda^b\kappa^b(T)]^{N^b}\cdots\cdots \\ &\times \frac{N!}{N^a!\,(N-N^a)!}\,\frac{(\alpha N^a)!}{N^b!\,(\alpha N^a-N^b)!}\cdots\cdots \\ &\times\exp\left[\left\{N^aE^a+N^bE^b\cdots\cdots+\frac{(N^a)^2}{N}E^{aa}\right.\right. \\ &\left.\left.+\frac{(N^b)^2}{\alpha N^a}E^{bb}\cdots\cdots\right\}\Big/kT\right] \qquad (1)\end{aligned}$$

where λ^a, $\lambda^b\cdots\cdots$ are the absolute activities of B molecules in sites of the *a*th, *b*th *etc.*, and $\kappa^a(T)$, $\kappa^b(T)$ *etc.* are the additional factors in the partition function per molecules for the contribution of B molecules

3) J. S. Anderson, *Proc. Roy. Soc.*, **A185**, 69 (1946).
4) A. L. G. Rees, *Trans. Faraday Soc.*, **50**, 335 (1954).

* In the present case, interstitial sites are assumed to arise from violanthrene lattice being made expansion. See the later section.

in the ath, bth *etc.* sites to the vibrational modes of the crystal. For the equilibrium state where $\partial\Theta/\partial N^a=0$, $\partial\Theta/\partial N^b=0$,

$$\lambda^a=\frac{1}{\kappa^a(T)}\frac{N^a}{(N-N^c)}\left\{1-\left(\frac{N^c}{\alpha N^a}\right)\right\}^{\alpha}\times\exp\left[\left\{-E^c-\frac{2N^a}{N}E^{aa}+\frac{1}{\alpha}\left(\frac{N^b}{N^a}\right)^2E^{bb}\right\}\Big/kT\right] \quad (2)$$

$$\lambda^b=\frac{1}{\kappa^b(T)}\frac{N^b}{(\alpha N^a-N^b)}\left\{1-\left(\frac{N^c}{\beta N^b}\right)\right\}^{\beta}\times\exp\left[\left\{-E^b-\frac{2N^b}{\alpha N^a}E^{bb}+\frac{1}{\beta}\left(\frac{N^c}{N^b}\right)^2E^{cc}\right\}\Big/kT\right] \quad (3)$$

etc.

In applying the theory to our results, we assume that the composition of $\overline{\mathrm{V}\cdot 2\mathrm{I}_2}$ (idealized formula) corresponds to that of the interstitial solid solution where the ath kind site is saturated and the other sites are completely empty. This means that the violanthrene lattice made of N_0 molecules has $2N_0$ sites of the ath kind for iodine molecules. In reality, however, n molecules of iodine occupy a part of $2N_0$ sites of the ath kind and some numbers of molecules occupy the sites of the bth, cth *etc.* kind. We have no foundation to assume the numbers of sites of the bth, cth *etc.* kind. However, in the range of composition where the total mole ratio of iodine to V is not greater than 2, it may not be far from the truth if we presume that the number of iodine molecules occupying the other sites is far less than the number of molecules occupying the ath kind sites. This leads to the assumption of $N^b/\alpha N^a\ll 1$ in eq. (2).

Introducing $\theta=n/2N_0$ instead of N^a/N in eq. (2), we obtain

$$\lambda(\theta)=\frac{1}{\kappa^a(T)}\frac{\theta}{1-\theta}\times\exp[-\{E^a+2\theta E^{aa}\}/kT] \quad (4)$$

for the activity of the iodine molecule in the ath site.

In the isotherm of Fig. 1, at the composition of mole ratio being 2, θ is not equal to unity, but less than unity for the reason mentioned above. Let θ be $\delta<1$ at the composition where total mole ratio is 2, then the relative activity at any composition can be expressed as

$$\frac{\lambda(\theta)}{\lambda(\delta)}=\frac{\theta}{1-\theta}\frac{1-\delta}{\delta}\times\exp[4(\delta-\theta)T_c^a/T] \quad (5)$$

where $T_c^a=-E^{aa}/2k$, which is the critical temperature above which two phase region should disappear.

Eq. (5) can be applied to the experimental data to delineate the isotherm. For this purpose, we assume $\lambda(\theta)/\lambda(\delta)=c(\theta)/c(\delta)$, where c is the concentration of iodine in carbon tetrachloride at the equilibrium. We further assumed that $\delta=0.87$, $c(\delta)=0.0105$ at -3°C; $\delta=0.84$, $c(\delta)=0.0220$ at 27°C and $T_c^a=260$°K. These values have been estimated to be as good as possible to be fitted to the observed values. The theoretical isotherms are shown by the curves in Fig. 1.

The agreement between the experimetal results and the theoretical calculations is satisfactory when we realize that the theory contains many approximations. This leads to the conclusion that "violanthrene-iodine complex" at room temperature is a solid solution between violanthrene and a non-stoichiometric molecular compound, which has the composition of $\mathrm{V}\cdot 2\mathrm{I}_2$ as the idealized formula and should be separated as a solid phase below the critical temperature of 260°K.

From the isotherms of 27°C and -3°C, the heat of dissociation of the complex can be calculated by Clapeyron's relation. This value is 3.8 kcal. per one mole of iodine for the complex having composition of mole ratio being 1 (where assumed $\theta=0.5$). The heat of dissociation depends on the composition in such a manner as expressed as $E^a+2\theta E^{aa}$. Therefore, this value corresponds to the mean heat of dissociation in the composition range from $\theta=0$ to $\theta=1$, where the interstitial sites of the ath kind have been completely occupied by iodine molecules. Alternatively one may say that the integral heat of dissociation of the complex having the composition of $\overline{\mathrm{V}\cdot 2\mathrm{I}_2}$ is 3.8 kcal. per mole of iodine. Then,

$$2\mathrm{I}_2(\text{in }\mathrm{CCl}_4)+\mathrm{C}_{31}\mathrm{H}_{18}(\text{solid})=\mathrm{C}_{31}\mathrm{H}_{18}\cdot 2\mathrm{I}_2(\text{solid})+7.6\text{ kcal.} \quad (6),$$

and, since the heat of dissolution of iodine in carbon tetrachloride is 5.8 kcal. per mole of iodine[5],

$$2\mathrm{I}_2(\text{solid})+\mathrm{C}_{31}\mathrm{H}_{18}(\text{solid})=\mathrm{C}_{31}\mathrm{H}_{18}\cdot 2\mathrm{I}_2(\text{solid})-4.0\text{ kcal.} \quad (7).$$

X-Ray Studies on Violanthrene-Iodine Complex

X-Ray studies were made by Norelco

5) K. Hartley and H. A. Skinner, ibid., 46, 621 (1950).

diffractometer with Ni-filtered Cu-K_α radiation. Typical diffractometer records of complexes having varied compositions are shown in Fig. 2.

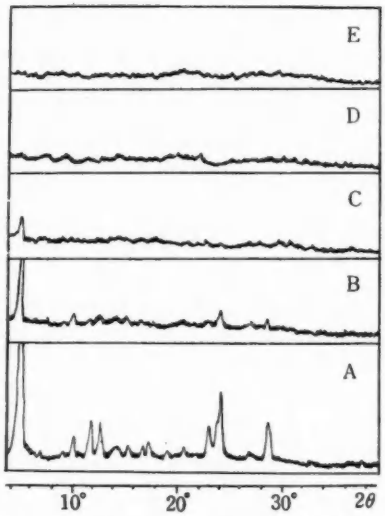

Fig. 2. Diffractometer record of violanthrene-iodine complex.
Mole ratio of iodine to violanthrene: A 0.12, B 0.40, C 1.48, D 2.27, E 4.69.

Sharp crystalline peaks are seen in the diffraction patterns of complexes which have a low content of iodine. These peaks coincide with the diffraction peaks of violanthrene crystal itself, and decrease their intensities as the mole ratio of iodine to V is increased. In this process, no change is found in either positions or the relative intensities of peaks, and no appearence of any other crystalline peaks can be found. These facts show the presence of non-reacted violanthrene crystallites in the specimen, and they also show that the main part which has combined with iodine becomes amorphous. As for the specimens, in which the mole ratio is greater than 2, crystalline peaks disappear completely.

The preliminary examination of violanthrene-bromine complex has also shown an amorphous pattern. However, both these cases seem to belong to the special cases. The complexes between polycyclic aromatic hydrocarbons and halogens are not necessarily amorphous. The complex of perylene or pyranthrene shows a clearly crystalline pattern. For instance, in the case of perylene-iodine complex two kinds of crystalline pattern are found in the same specimen; one is probably due to molecular compound between one molecule of perylene and one of iodine, and the other to one molecule of perylene and two of iodine. This fact makes the analysis of the diffraction pattern of this complex complicated. On the other hand, the violanthrene-iodine system gives a completely amorphous pattern and is suited for the application of the radial-distribution analysis. For this purpose, it is desired that the specimen will have enough iodine content to give a completely amorphous structure, but not such an excess in amount as to separate iodine crystals. An intensity distribution curve of scattered X-rays by the complex is shown in Fig. 3.

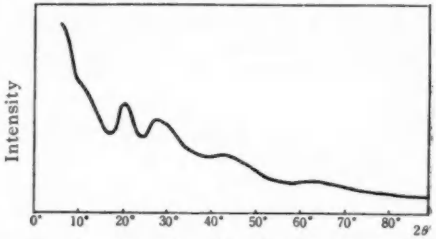

Fig. 3. Intensity distribution curve of violanthrene-iodine complex (1 : 4.9)

Radial-Distribution Analysis

The intensity, I, of scattering in the direction of 2θ (scattering angle) is given by the theory[6] as

$$I=\sum_i f_i^2+\sum_i\sum_j f_i f_j \frac{\sin sr_{ij}}{sr_{ij}},$$
$$s=\frac{4\pi \sin\theta}{\lambda} \qquad (8)$$

where r_{ij} is the distance between the i-th and j-th atoms, f is the atomic scattering factor, and λ the wave length of the X-ray. In the case where the specimen contains more than one kind of atom, the general formula for the intensity of scattering can be written[7] as,

$$I=N\sum_p f_p^2+\sum_m^{m\neq n}\sum_n f_m f_n \cdot \frac{\sin sr_{mn}}{sr_{mn}} \qquad (9)$$

where m, n,..... denote the kinds of atom constituting an appropriate unit of structure of which the entire specimen is

6) P. Debye, *Ann. Physik*, **46**, 809 (1915).
7) B. E. Warren, H. Krutter and O. Morningstar, *J. Am. Ceram. Soc.*, **19**, 202 (1936); H. P. Klug and L. E. Alexander, "X-Ray Diffraction Procedures" John Wiley and Sons, Inc., 1954, p. 590.

regarded as being composed, and N is the number of such units.

Let the average numbers of atoms lying at $r \sim r+dr$ from the reference atom be a_m, a_n, *etc.*, and let the atomic density function $\rho_m(r)$ which is defined by eq. (10) be used; then eq. (9) can be expressed as eq. (11),

$$4\pi r^2 \rho_m(r)dr = \sum_m a_m f_m \tag{10}$$

$$I = N\left[\sum_m f_m^2 + \sum_m f_m \int 4\pi r^2 \rho_m(r) \frac{\sin sr}{sr} dr\right] \tag{11}$$

The following approximations are introduced,

$$f_m = K_m f_e \tag{12}$$

$$\rho_m(r) = f_e g_m(r) \tag{13},$$

where f_e is the scattering factor of a single electron, K_m is the effective number of electrons per atom of type m, and $g_m(r)$ is the electron-density function. Using those approximations, eq. (11) is expressed as

$$I = N\left[\sum_m f_m^2 + 4\pi f_e^2 \int \sum_m K_m g_m(r) r^2 \frac{\sin sr}{sr} dr\right] \tag{14}$$

Finally, introducing g_0, the average density of electrons in the specimen, eq. (14) can be transformed to eq. (15) by means of the Fourier integral theorem.

$$4\pi r^2 \sum_m K_m \cdot g_m(r) = 4\pi r^2 \cdot g_0 \cdot \sum_m K_m + \frac{2r}{\pi} \int_0^\infty s \cdot i(s) \cdot \sin sr \cdot ds \tag{15}$$

in which

$$i(s) = \left(\frac{I}{N} - \sum_m f_m^2\right) / f_e^2 \tag{16}$$

From the observed intensity curve of scattering, the radial-distribution function, $4\pi r^2 \sum_m K_m g_m(r)$, can be obtained by eq, (15).

The approximation of eq. (12) is possible only in the case where the specimen is made of atoms whose atomic numbers are near to each other. In the cases of iodine and carbon, their atomic numbers are far from each other. However, since the atomic number of iodine is much larger than that of carbon, in such a composition as that of one molecule of violanthrene and five of iodine, it has been revealed that the intensity of coherent scattering is determined mainly from the contribution of iodine atoms. In such a case, the above approximation is again allowed.

We assume the structure unit as $I \cdot (C_{34}H_{18})_{0.1}$ for the complex made of one molecule of violanthrene and five molecules of iodine, and the effective numbers of electrons being one for hydrogen, 6 for carbon and 53 for iodine atom. From the observed density, $d=3.03$, $g_0 = 0.602d \times \sum_m K_m / \sum_m M_m$, where M_m is the atomic weight, is given as 0.809 electrons per Å^3.

The integral in eq. (15) is replaced by the equivalent summation,

$$\int_0^\infty s \cdot i(s) \cdot \sin sr \cdot ds = \sum_{s=0}^{s=s_{max}} s \cdot i(s) \cdot \sin sr \cdot \Delta s \tag{17}$$

and the computation has been made, giving $\Delta S = 0.04\pi$, for every interval of 0.2 Å for r. The radial-distribution function obtained is shown in Fig. 4.

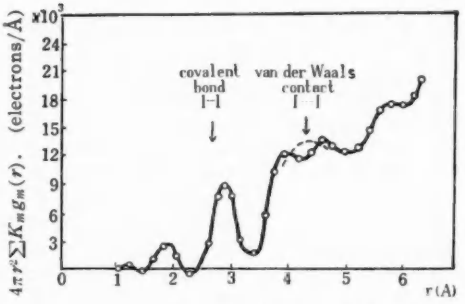

Fig. 4. Radial distribution curve of violanthrene-iodine complex (mole ratio 1 : 4.9).

The radial-distribution curve has a remarkable maximum at $r=2.85$ Å. This peak is clearly resolved and encloses an area of 3500 electrons. If this peak is due to the coherent scattering between carbon atoms in a violanthrene molecule, the area will be $(34/10) \times 3 \times 6^2 = 368$ electrons, since the statistical average number of carbon atoms surrounding a reference carbon atom at the distance of 2~3 Å is 3. This can not explain the above large area of the peak. On the other hand, I-I distance in an iodine molecule is 2.667 Å from optical data, and 2.70 Å from the analysis of crystal structure. If we assume that the peak is due to the interaction between iodine atoms in an iodine molecule, the area will be $1 \times 53^2 = 2800$ electrons. The summation of the effects due to iodine molecule and violanthrene molecule can almost explain the area under the peak. However, it is clear that the

most part of the effect arises from the contribution of the iodine molecule. From this, it is revealed that most iodine molecules do not dissociate into ions, but I-I distance is extended to 2.85 Å.

In the region of r=4~5 Å, two maxima are seen. They are rather poorly resolved. In eq. (17), the upper limit, ∞, of the integral is replaced by a finite value, s. This procedure leads to the result of the so-called termination error[8]. In our case, the termination effect due to the major peak at r=2.85 Å will result in the appearance of subsidiary maxima at r=1, 1.8, 3.7 and 4.5 Å, and minima at r=1.5 and 4.2 Å. In Fig. 4, two small maxima at 1~2 Å may be due to this termination error. Therefore, the similar effect is also presumed in the region of 4~5 Å. The true distribution curve seems to be shown by a dotted line in Fig. 4. The maximum, ranging from 3.5 to 5.5 Å, encloses an area of about 16500 electrons.

In a violanthrene molecule, the average number of carbon atoms surrounding a reference atom at the distance of 3.5~5.5 Å is not more than 5. It is clear that the observed area can not be explained by the interaction between these carbon atoms. The distance of 3.5~5.5 Å corresponds to the distance between iodine atoms which make van der Waals contact with each other. In iodine crystal, from a reference atom there are 2 atoms at 3.6 Å, 8 at 4.4 Å, 2 at 4.8 Å, and 1 at 5.1 Å, i.e., 13 atoms at the distance of this range. If the maximum arises due to the interaction between these iodine atoms, the area should be $13\times53^2=36400$ electrons, which is much larger than the observed area. Therefore, the observed area is not explained by the arrangement of iodine molecules as that in iodine crystal. It appears that an atom should be surrounded by 5~6($=16500/53^2$) atoms. This suggests the presence of small groups of iodine molecules presumably in two dimensional arrangement.

Density of Violanthrene-Iodine Complex

The density measurement was made with a pycnometer. Carbon tetrachloride solution of iodine which is in equilibrium with complex was used as the liquid medium. The results are shown in Fig. 5, where specific volumes of complexes are plotted against compositions. It has been found that the specific volume of a complex is larger than the sum of the specific volumes of its constituents, in the region up to the mole ratio of 2.5. Beyond this mole ratio, the volume becomes additive. This result suggests that, at an early stage of the complex formation, in the range of low iodine content, violanthrene molecular lattice is expanded and the structure with vacant space is produced. As iodine content increases, the vacancies are gradually occupied by iodine molecules and filled up at the concentration where the total mole ratio becomes 2.5. This is clearly seen in the change of partial molal volume of iodine in this system.

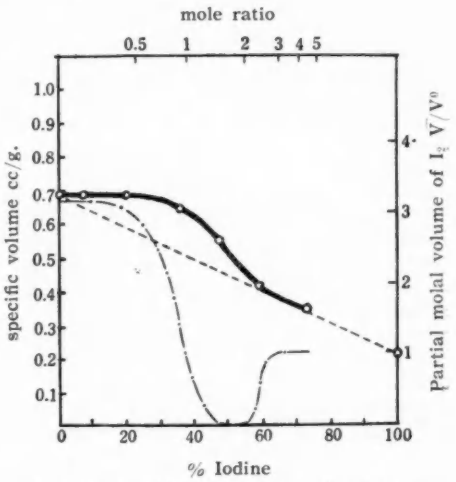

Fig. 5. Specific volume of voilanthrene-iodine system ——, and partial molal volume of iodine in the same system —·—.

The analysis of crystal structure has not yet been made for violanthrene. However, the crystal structures of many kinds of polycyclic aromatic hydrocarbon have been studied by Robertson[9]. The analogy suggests that (001) plane will be the cleavage plane in violanthrene lattice as in other crystals of polycyclic hydrocarbons. If it is so, it will be most facile for iodine molecules to penetrate into interstices between (001) planes. This will lead to the expansion of the crystal in the c-axis direction. However, as mentioned in the preceding section, there is no sign of any preferential change of crystal structure in the complex formation, but the whole structure becomes amorphous. Therefore,

8) W. L. Bragg and J. West, *Phil. Mag.*, **10**, 823 (1930).

9) J. M. Robertson, "Organic Crystals and Molecules", Cornell Univ. Press., Ithaca, N. Y., 1953, p. 183.

it may be concluded that iodine molecules do not penetrate into interstices between the preferential crystal plane, but wedge themselves directly between the molecules of violanthrene.

The molecular volume of violanthrene is about five times as large as that of iodine, and the surface of a violanthrene molecule can be occupied by 5~6 iodine molecules. Therefore, as the result of penetration of an iodine molecule between two neighboring violanthrene molecules, a large vacant space is produced. It is noteworthy that the vacancies are filled up by iodine molecules at the composition where the total mole ratio is 2.5, which is a larger value than the composition corresponding to $V \cdot 2I_2$. From this it is most plausible to assume that the complex, having the composition of $V \cdot 2I_2$, has the structure in which 4 iodine molecules are sandwiched between two neighboring molecules of violanthrene.

Such a model is consistent with the result of the radial-distribution analysis which indicates that an iodine atom is surrounded by statistically 5~6 iodine atoms in van der Waals contact. It is also not inconsistent with the assumption which has been made in the thermodynamical treatment. What we called the *a*th site before can be made to correspond to the site which can be occupied by 4 molecules of iodine between two neighboring violanthrene molecules.

Summary and Discussion

From the thermodynamical consideration on the isotherm of the violanthrene-iodine system, it was revealed that the system can be seen an interstitial solid solution. Up to the point where the mole ratio is 2, the solid solution is the one between violanthrene and a molecular compound. The latter has no stoichiometric composition, but consists of approximately one violanthrene molecule and two iodine molecules, and can be written as $V \cdot 2I_2$ in the idealized formula. Beyond the above mole ratio, the solid solution is the one presumably between $V \cdot 2I_2$ and iodine. The radial distribution analysis of X-ray diffraction also supports the entity of the molecular complex $V \cdot 2I_2$.

The heat of formation in eq. (6) or eq. (7) is a roughly estimated value. There is a great deal of information on the heat of formation of the molecular compounds of iodine. For instance, the heat of formation of molecular compound between pyridine and iodine dissolved in pyridine was presumed to be 7.95 kcal[5]. In eq. (6), if we consider the heat of dissolution of violanthrene which is presumably a larger one, the heat of complex formation between iodine and violanthrene molecules should have a much larger value than 7.6 kcal.

The heat of formation, in eq. (7), among the solid phases is endothermic. However, a large amount in entropy change will be expected and it will cover the heat of formation to gain the free energy for complex formation. In reality, when violanthrene crystalline powder is brought into contact with iodine the solid complex is formed spontaneously.

From the radial-distribution analysis, it was revealed that, after the complex formation, the interatomic distance of an iodine molecule is extended to 2.85 Å from 2.67 Å of normal iodine molecule. G. Dallinga[10] reported that in pyridine solution of iodine the I-I distance is increased to 2.90 Å. This value is comparable to our case. If we assume the intermolecular charge-transfer force for the complex formation, an electron will be transferred from violanthrene to iodine molecule, getting into the anti-bonding orbital. This will lead to an increase in the I-I distance according to the degree of contribution of the dative structure $\phi(V^+ - I_2^-)$. However, we can not get any single solution for the ionic character of iodine molecule from its interatomic distance alone.

It was concluded from the density measurement, that the molecular complex of $V \cdot 2I_2$ has the structure in which iodine molecules are sandwiched between two neighboring violanthrene molecules. If this is true, such a structure is one of the characteristics of this system, with the facts that the molecular compound is not stoichiometric in its nature and that the system as a whole is amorphous, and is very similar to the molecular compounds of graphite. It is not known in detail how iodine molecules are arranged in relation to hydrocarbon molecules. However, the above structure suggests strongly that each iodine molecule is not localized preferentially to a fixed position of violanthrene molecule, but occupies the sites rather freely with a diffuse interaction force.

10) G. Dallinga, Abstract of paper at the 3rd. Congress of International Union of Crystallography, cf. *Acta Cryst.*, **7**, 665 (1954).

Such a structure like this is frequently seen amongst the intermediate phases of metallic system and among the quasi-metallic compounds. It is most interesting to see such a structure in an organic substance which has a high electrical conductivity.

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Department of Chemistry, Faculty of Science, The University of Tokyo
Hongo, Tokyo

On Mangiferin, the Coloring Matter of Mango (Mangifera indica Linn.). IV[1]. Isolation of 1,3,6,7-Tetrahydroxyxanthone and the Skeletal Structure of Mangiferin[2]*

By Syun ISEDA

(Received March 9, 1957)

In Part III[1] of this series, it was shown that mangiferin is a substance agreeing with the composition $C_{19}H_{18}O_{11}$. For the structure of this pigment, Wiechowski[3] proposed a formula having a skeleton of 1,4,5,7-tetrahydroxyxanthone, but failed to offer any evidence supporting such an assumption. The fact that mangiferin changes into euxanthic acid in rabbit body[3] indicates that the pigment molecule possesses a xanthone skeleton or a structure that can easily resume the xanthone skeleton, and Gorter[4] proposed a structural formula favoring the latter. Although structural formulae were proposed, all attempts for the experimental evidence of skeletal structure of the pigment molecule have been unsuccessful.

Mangiferin resists hydrolysis with hydrochloric or sulfuric acid and the "genin" can not be isolated by such a method. Wiechowski[3] tried the application of hydroiodic acid but has not isolated any crystalline product. The writer succeeded in isolating a crystalline product by heating the pigment in phenol with hydriodic or hydrobromic acid.

This product was not found to be purifiable *per se* when it was acetylated, and the acetate was recrystallized from glacial acetic acid to colorless crystals, $C_{21}H_{16}O_{10}$, m.p. 200°C. Hydrolysis of this acetate with an acid afforded a product (I) as pale yellow crystalline powder or microneedle crystals, which colored markedly at 320°C, became brown at around 350°C and decomposed at 370–371°C. The analytical values agreed with $C_{13}H_8O_6$. This compound showed its phenolic property by coloring green with ferric chloride. The crude decomposition product melted with decomposition at 368°C before acetylation and its ultraviolet absorption spectrum agreed practically with that of I, recovered from the purified acetyl derivative; it is therefore certain that no cyclization or other changes in the molecular structure had taken place during acetylation.

Methylation of I with diazomethane gives a derivative (II), $C_{16}H_{14}O_6$, m.p. 218–219°C, which indicates the presence of a free phenolic hydroxyl by the positive ferric chloride reaction. Its acetylation gives crystals of m.p. 216°C, $C_{15}H_{16}O_7$, negative to the ferric chloride test, but its hydrolysis reverts it to II, m.p. 218–219°C. Application of diazomethane to II results in the total recovery of the unchanged II. It follows, therefore, that I contains a phenolic hydroxyl that is not methylated with diazomethane.

The melting points and the analytical

* *Mangiferine*, used to date, is hereafter corrected to *mangiferin* in accordance with international nomenclature.

1) Part III: S. Iseda, *J. Kumamoto Women's Univ.*, **9** (1957), in press. (in Japanese).

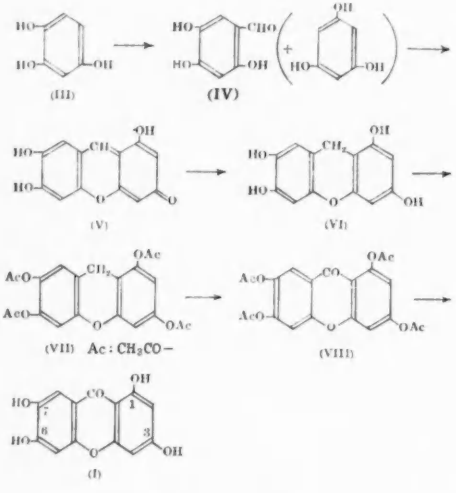
2) Presented at the Kyushu Local Meeting of the Chemical Society of Japan, Kumamoto, December 26, 1956.

3) W. Wiechowski, *Arch. exp. Pathol. Pharmakol.*, **97**, 462 (1923).

4) K. Gorter, *Bull. Jardin Bot. Buitenzorg*, (iii) **4**, 260 (1922).

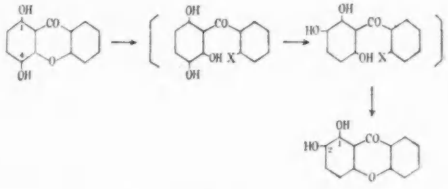
values of the acetyl derivative of I and those of II are respectively identical with the values[5] of 1,3,6,7-tetraacetoxyxanthone, m.p. 198°C, and 1-hydroxy-3,6,7-trimethoxyxanthone, m.p. 216°C. However, the melting point of 1,3,6,7-tetrahydroxyxanthone, thought to be identical with I, is given in the literature[5,6] as decomposing at 320°C. Through the courtesy of Prof. Shoji Shibata of University of Tokyo, a sample synthesized by Tanase[5] was made available. Mixed samples of the acetates and methyl ethers failed to show any depression of the melting point. The phenol also showed the same behavior when the synthetic product alone or in admixture with I was fused.

Since the Tanase sample was about 15 years old, a product was synthesized for comparison. Tanase reported two routes for the preparation of 1,3,6,7-tetrahydroxyxanthone. Hatsuda and Kuyama[6] reported the synthesis of 1,3,6,7-tetrahydroxyxanthone, m.p. 320°C(decomp.), by the preparation of diphenyl ether from 4-bromoveratrole and phloroglucinol dimethyl ether by the Ullmann reaction, according to Tanase's method, and then by deriving it to xanthone derivative by the application of oxalyl chloride. The writer carried out the synthesis by the second method (Scheme 1) and the product thereof was identical with the natural product, decomposing at 370°C. Since Tanase had observed that the products obtained by the two methods of synthesis are identical, the value of m.p. 320°C (decomp.) must indicate the initial browning temperature of the product.



Scheme 1

Heating of some kinds of flavone with hydroxyl group with hydriodic acid often causes rearrangement of the hydroxyl and this phenomenon is called the Wessely-Moser rearrangement[7]. This phenomenon has been observed in xanthones[8] and its mechanism is explained as follows (Scheme 2):



Scheme 2

As will be clear from this mechanism, the rearrangement changes the hydroxyls in 1,4-positions to 1,2-positions (the reverse of this has not been observed). Therefore, the hydroxyl in 3-position is independent of this rearrangement and the rearrangement does not occur if there has been no hydroxyl in 1-position from the beginning. Considering such a mechanism, 1,3-dihydroxyxanthone would give a product with the same structure and 2,3-dihydroxyxanthone can not undergo such a rearrangement. Therefor, 1,3,6,7-tetrahydroxyxanthone can not be formed by rearrangement from other isomers. In other words, 1,3,6,7-tetrahydroxyxanthone must have been present in the pigment molecule from the beginning.

Next, considerations will be made on the possibility of a cyclization by the action of hydriodic acid where no xanthone ring was present in the pigment molecule itself. Since there is no possibility of a formation of a new benzene ring by the

5) Y. Tanase, *J. Pharm. Soc. Japan*, **61**, 341 (1941).
6) Y. Hatsuda and S. Kuyama, *J. Agr. Chem. Soc. Japan*, **29**, 14 (1955).
7) F. Wessely and G. H. Moser, *Monatsh.*, **56**, 97 (1930); F. Wessely and F. Kallab, ibid., **60**, 26 (1932); S. Hattori, *Acta Phytochim.*, **5**, 99,117,219 (1930); *J. Chem. Soc. Japan*, **50**, 725 (1929); **51**, 570 (1930); Ber., **72**, 1914 (1939); R. C. Shah, C. R. Mehta and T. S. Wheeler, *J. Chem. Soc.*, **1938**, 1555.
8) E. M. Philbin, J. Swirski and T. S. Wheeler, *Chem. & Ind.*, **1955**, 445.

action of hydriodic acid**, the point to be considered would be the γ-pyrone ring in the center. In such a case, there will be the diphenyl ether structure with the ketone portion severed and a benzophenone structure with the ether linkage severed. As the latter example, there is sulochrin[9], isolated from the mycelium of *Oospora sulphurea-ochracea*. If mango pigment belongs to the latter group, it must be a hexahydroxybenzophenone compound in order to cyclize into tetrahydroxyxanthone derivative. If such is the case, application of diazomethane must afford a tetramethyl ether, even if two hydroxyls will not be methylated due to a substituent and the chelation to the carbonyl group. However, the pigment only affords a dimethyl ether even when sufficient diazomethane reacted. Since there is no methoxyl group in the pigment itself and the color reaction denies*** the partial structure of *ortho*- and *para*-diphenols, the possibility of a benzophenone derivative for the pigment is excluded.

If the pigment is a diphenyl ether derivative, there must be one carboxyl radical *ortho* to ether linkage, but the infrared spectra*** of the pigment and its methyl derivative do not indicate the presence of a carboxyl or an ester-carbonyl group. It therefore follows that the pigment can not be a diphenyl ether derivative. The fact that the ultraviolet absorption spectrum (Fig. 1) of mangiferin is quite similar to that of 1,3,6,7-tetrahydroxyxanthone supports the presence of such a structure in the pigment molecule.

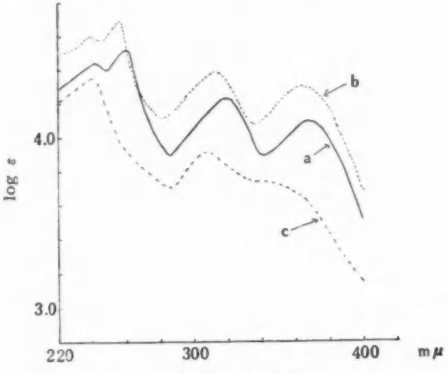


Fig. 1. Ultraviolet absorption spectra of mangiferin (a: ——), 1,3,6,7-tetrahydroxyxanthone (b: ·····), and its tetraacetate (c: – – –).

The known tetrahydroxyxanthone compounds isolated to date from natural substances may be found in the 1,3,5,8-isomer obtained from swertianolin or its aglycone, swertianol, isolated from *Swertia japonica Makino*[10] and *S. tomentosa Makino*[11] of Gentianaceae, and the 1,3,5,6-isomer[12] obtained as the oxidation product of jacareubin, the pigment of the heartwood of *Calophyllum brasiliensis* Camb. of Guttiferae. The skeletal compound of swertinin and decussatin, the pigments of *Swertia decussata*, is said to be the 1,2,6,8-isomer from absorption spectra[13]. The presence of a 1,3,6,7-isomer in natural substances to be the first example and this would be also the first example of a xanthone derivative in plants belonging to Anacardiaceae.

The writer expresses his gratitude to Professor Ryozo Hirohata of the Kyushu University, for his kind guidance and encouragement throughout the course of this work, to Professor Shoji Shibata of the Pharmaceutical Institute, University of Tokyo, for kind supply of a valuable sample, to Professor Yaichiro Tanase of the Pharmaceutical Faculty, Tokushima University, for kind advice and the supply of literature, to Professor Eigai Sebe of the Kumamoto University Medical School for kind help in analysis, and to Dr. Keihei Ueno of the Dojin Pharmaceutical Laboratory for ultraviolet spectral measurements. The writer is also indebted to Mr. Eikichi Aoyagi of the Miike Dye Industries, Oomuta, for elementary analyses.

Experimental

Unless otherwise noted, all melting and decomposition points are corrected.

Action of Hydriodic Acid on Mangiferin.—To 30 g. of phenol, 5.0 g. of finely pulverized mangiferin was added and mixed with warming (remains practically insoluble). While cooling, 50 cc. of hydriodic acid (*d* 1.7) was added

** There is a report [A. Mustafa and M. I. Ali, *J. Org. Chem.*, **21**, 849 (1956)] on the formation of a tetrahydroxanthone by the new formation of a cyclohexene ring in diene synthesis.

9) H. Nishikawa, *Bull. Agr. Chem. Soc. Japan*, **12**, 47 (1936); **13**, 1 (1937). *Acta Phytochim.*, **11**, 167 (1939).

*** See the forthcoming report, Part V.

10) Y. Asahina, J. Asano and Y. Ueno, This Bulletin, **17**, 104 (1942); *J. Pharm. Soc. Japan*, **62**, 22 (1942).

11) T. Nakaoki and Y. Hida, *J. Pharm. Soc. Japan*, **63**, 554 (1943).

12) F. E. King, T. J. King and L. C. Manning, *J. Chem. Soc.*, **1953**, 3932.

13) S. R. Dalal, S. Sethna and R. C. Shah, *J. Indian Chem. Soc.*, **30**, 457, 463 (1953); R. C. Shah, A. B. Kulkarni and S. R. Dalal, *J. Sci. Ind. Research*, **13B**, 175 (1954).

gradually and the mixture was gently refluxed for 6 hours. When cooled, the two-layered mixture was poured into an aqueous solution of sodium bisulfite with agitation and the dark brown, resinous substance that separated was washed thoroughly with water. This resinous substance was boiled with four 500-cc. portions of water, the oily substance insoluble in hot water was collected by filtration, and the cooling of the filtrate afforded a pale brown precipitate. Yield, 2.5 g. of m.p. 368–370°C (decomp.). Ferric chloride reaction: Dusky greenish black.

Action of Hydrobromic Acid on Mangiferin.—Application of hydrobromic acid (constant boiling product) under exactly the same conditions as for hydriodic acid, or even without the addition of phenol, 1,3,6,7-tetrahydroxyxanthone was isolated, though in a smaller yield. In the case of an application of the acid alone, without phenol, the pigment dissolved in hydrobromic acid on heating the mixture in an oil bath and a black insoluble matter separated out immediately. After cooling, the insoluble matter was collected, the portion soluble in ethyl acetate was acetylated, and the product was recrystallized from glacial acetic acid to 1,3,6,7-tetra-acetoxyxanthone, m. p. 200°C. Yield, 15–20% of the original pigment.

1,3,6,7-Tetra-acetoxyxanthone.—Two grams of the substance of m.p. 368–370°C, soluble in hot water, obtained by the application of hydriodic acid to the pigment, was acetylated by heating with acetic anhydride and a drop of conc. sulfuric acid for 4 hours. This was decomposed by the addition of water, the precipitate was collected, washed with water, and dried. Five recrystallizations from as small an amount as possible of glacial acetic acid, twice using activated carbon, afforded colorless, long prisms m.p. 199.5–200°C, Yield, 1.6 g. Ferric chloride reaction: Negative. It precipitates out as thick, rhombic plates from hot saturated acetone solution but forms fine needles when the acetone solution is allowed to evaporate or when recrystallized from ethanol, but no difference in the melting point was observed in either case.

Anal. Found: C, 58.97, 59.13; H, 4.17, 3.88. Calcd. for $C_{21}H_{16}O_{10}$: C, 58.88; H, 3.77%.

No depression of the melting point was observed on admixture with the synthesized 1,3,6,7-tetra-acetoxyxanthone, m.p. 198°C. It can be obtained by direct acetylation of the resinous substance obtained on decomposition with hydriodic acid, without extraction with hot water, but the yield is poor.

1,3,6,7-Tetrahydroxyxanthone.—A mixture of 350 mg. of the tetra-acetate, m.p. 199.5–200°C, in 20 cc. of ethanol containing 5 cc. of conc. hydrochloric acid was refluxed for 5 hours, the solvent was evaporated under a reduced pressure, and water was added to the bright yellow residue. The pale yellow mass (290 mg.), obtained on washing this residue with water and drying, was dissolved in 4 cc. of ethanol, filtered, and brought to 10 cc. with hot water. On cooling this solution, pale brown needles or a crystalline powder was obtained, which became slightly brownish at around 320°C, became brown colored at around 350°C, and blackened with decomposition at 370–371°C. It is easily soluble in acetone and ethanol and sparingly in ether. Air-dried product gave analytical values almost corresponding to $C_{13}H_8O_6 \cdot H_2O$.

Anal. Found: C, 55.72; H, 4.01. Calcd. for $C_{13}H_8O_6 \cdot H_2O$: C, 56.12; H, 3.62%.

Sample dried for 10 hours in vacuo at room temperature.

Anal. Found: C, 59.89; H, 3.20. Calcd. for $C_{13}H_8O_6$: C, 60.01; H, 3.20%.

The melting point determination of the synthesized 1,3,6,7-tetrahydroxyxanthone[5] alone or in admixture with the foregoing product gave the same results as above.

1-Hydroxy-3, 6, 7-trimethoxyxanthone.—Ether solution of diazomethane made from 2.0 g. of nitrosomethylurea was added to a suspension of 0.1 g. of 1,3,6,7-tetrahydroxyxanthone in 20 cc. of ether, by which the phenol gradually disappeared with evolution of bubbles. After 5 hours, the residual diazomethane was decomposed by the addition of a few drops of glacial acetic acid, the solvent was evaporated, and the residue was dissolved in 30 cc. of 5% potassium hydroxide solution. This solution was continuously extracted with ether for 10 hours, and the colorless ether extract was evaporated, leaving 90 mg. of a pale yellowish brown residue. Recrystallization from dilute ethanol afforded pale yellowish brown microneedles, m.p. 218–219°C. They dissolve in conc. sulfuric acid to form a bright yellow solution with green fluorescence. It colors green gradually with ferric chloride.

Anal. Found: C, 63.50; H, 4.72. Calcd. for $C_{16}H_{14}O_6$: C, 63.56; H, 4.67%.

Mixed m.p. with the synthesized 1-hydroxy-3,6,7-trimethoxyxanthone, m.p. 216°C[5], was 218°C.

1-Acetoxy-3, 6, 7-trimethoxyxanthone.—Acetylation of 0.1g. of 1-hydroxy-3,6,7-trimethoxyxanthone with acetic anhydride and a drop of conc. sulfuric acid gave 0.1 g. of a crude product, which was treated with a small amount of acetone to remove a minute amount of soluble pale yellow substance. Recrystallization of the residue from ethanol afforded fine prisms, m.p. 216°C. Ferric chloride reaction, negative.

Anal. Found: C, 62.81; H, 4.75. Calcd. for $C_{18}H_{16}O_7$: C, 62.79; H, 4.68%.

Mixed m.p. with 1-hydroxy-3,6,7-trimethoxyxanthone, m.p. 218–219°C, was 180–195°C. Admixture with mangiferin dimethyl ether acetate, m.p. 216–217°C, melted at 190–205°C. Hydrolysis with ethanolic hydrochloric acid gave 1-hydroxy-3,6,7-trimethoxyxanthone.

Synthesis of 2,4,5-Trihydroxybenzaldehyde.—The hydroxyhydroquinone triacetate, obtained by the acetylation of benzoquinone, was hydrolyzed with ethanolic sulfuric acid, concentrated under a reduced pressure, and the residue, to which a small amount of water was added, was extracted with ether, from which hydroxyhydroquinone (III) was obtained. Twenty grams of (III) was dissolved in 200°cc.

14) Ref. 5 and L. Gattermann and M. Köbner, *Ber.*, **32**, 278 (1899).

of ether; 30 g. of freshly prepared zinc cyanide was added, and dry hydrogen chloride gas was bubbled through this solution. Ether was then evaporated, 120 cc. of water was added to the residue, and the mixture was warmed for 5 minutes. After cooling, the mixture was allowed to stand in an ice chest over night and the crystals that precipitated out were removed by filtration. The mother liquor was extracted with ether, ether was evaporated, and the residue crystallized on standing, without recrystallization, to 2,4.5-trihydroxybenzaldehyde IV as pale brown, long prisms, m.p. 229–230°C (decomp.). Yield, 20 g.

Anal. Found: C, 54.45; H, 4.28. Calcd. for $C_7H_6O_4$: C, 54.42; H, 4.11 %.

Synthesis of 1,3,6,7-Tetrahydroxyxanthone.—A solution of 7.3 g. of IV and 7.5 g. of phloroglucinol dissolved in 50 cc. of glacial acetic acid was mixed with 20 cc. of conc. hydrochloric acid, heated on a sand bath for 30 minutes, allowed to stand over night, and the reddish solid thereby formed was collected by filtration. The solid was washed consecutively with water, sodium bicarbonate solution, and water, and dried, affording 10 g. of 1,6,7-trihydroxyfluorone V. Without purification, this was mixed with 500 cc. of ethanol, mixed with 4 g. of 5 % palladium-charcoal and shaken in a hydrogen stream by which 1 l. of hydrogen was absorbed in 1.5 hours, the solution becoming almost colorless. The catalyst was filtered off and the filtrate was evaporated completely to dryness under a reduced pressure, affording 7.3g. of crude 1,3,6,7-tetrahydroxyxanthene VI. This was directly acetylated and treated by the usual method. Recrystallization of the product from a large amount of ethanol gave 7.5 g. of 1,3,6,7-tetra-acetoxyxanthene (VII), m.p. 177°C.

To a solution of 7.5 g. of VII, dissolved in a mixture of 50 cc. of glacial acetic acid and 30 cc. of acetic anhydride, 2.4 g. of chromium trioxide was added in small portions with shaking. After completion of the addition, the mixture was heated in a water bath for 3 hours, a large amount of water was added to the mixture, and the insoluble matter was recrystallized four times from glacial acetic acid to 5.5 g. of 1,3,6,7-tetra-acetoxyxanthone VIII, as colorless needles, m.p. 200°C, showing no depression on admixture with the product isolated from the natural substance.

Anal. Found: C, 58.78; H, 3.85. Calcd. for $C_{21}H_{16}O_{10}$: C, 58.88; H, 3.77 %.

This tetra-acetate VIII was hydrolyzed with an acid and the product was recrystallized from 30 % ethanol. The pale yellowish brown, crystalline powder thereby obtained gradually colored from around 320°C, became markedly brown at around 350°C, and decomposed with blackening at 370–371°C, the behavior being identical with that of 1,3,6,7-tetrahydroxyxanthone from the natural source.

Anal. Found: C, 59.88; H, 3.22. Calcd. for $C_{13}H_8O_6$: C, 60.01; H, 3.10 %.

Ultraviolet Absorption Spectra.—Measurements were made with the Beckman Model DU spectrophotometer of mangiferin in 70 % ethanol and 1,3,6,7-tetrahydroxyxanthone and its tetra-acetate in methanol.

Department of Chemistry, Kumamoto Women's University, Kumamoto

On Mangiferin, the Coloring Matter of Mango (Mangifera indica Linn.). V.[1] *Identification of Sugar Component and the Structure of Mangiferin*[2]

By Syun ISEDA

(Received April 11, 1957)

From the results previously[1,3] reported, it has become clear that mangiferin agrees with the composition of $C_{19}H_{18}O_{11}$ and includes a 1,3,6,7-tetrahydroxyxanthone skeleton ($C_{13}H_8O_6$). The difference in the molecular formula $C_6H_{10}O_5(+H_2O)$ coincides with a hexose group. Wiechowski[4] already proved the formation of levulinic acid by boiling the "mangin" with hydrochloric acid for a long time and indicated the possible presence of a sugar moiety, but failed to isolate the sugar. Gorter[5] proposed a structure containing a glucuronic acid group, but did not isolate it. The present writer also attempted the detection of sugars as described in the first paper of this series[6], but did not obtain any concrete result.

1) Part IV: This Bulletin, **30**, 625 (1957).
2) Paper presented at the Kyushu Local Meeting of the Chemical Society of Japan, in Fukuoka, November 24, 1956.
3) S. Iseda, *J. Kumamoto Women's Univ.*, **9**, 45 (1957).
4) W. Wiechowski, *Arch. exptl. Pathol. Pharmakol.*, **91**, 462 (1923).
5) K. Gorter, *Bull. Jardin Bot. Buitenzorg*, [III]. **4**, 260 (1922).
6) S. Iseda and T. Asai, *J. Med. Assoc. Formosa*, **38**, 447 (1939).

Application of periodic acid to the pigment in water results in coloration of the solution to reddish brown, indicating the liberation of iodine, but the consumption of periodic acid varied between 1 and 3 moles and definite values were not obtained. Steam distillation of this aqueous reaction mixture failed to show the presence of formaldehyde in the distillate. Direct distillation of this reaction mixture showed, however, the presence of formaldehyde in the distillate, though in an amount about 1/20 of the calculated. It is known that glucose or glucosides does not form formaldehyde by periodate oxidation[7] and since there is a consumption of periodic acid without the virtual formation of formaldehyde, it seems certain that the $C_6H_{10}O_5$ residue bonded to the xanthone skeleton is not a hexitol ether type.

The sugar is not split off when the pigment is heated with sulfuric or hydrochloric acid under ordinary pressure or with water under high pressure, but when it is heated with 1% or 10% sulfuric acid under high pressure at 140°C, and the aqueous solution of the product is extracted with ether* after deionization, a spot appears on the paper chromatogram of the aqueous solution. This spot was identical with that of glucose. It does not appear, when the heating conditions, such as temperature and duration, are different from those indicated above. This experiment makes it certain that there is a glucose in the mangiferin molecule, but how and why that sugar is not split off by ordinary method is not clear.

Infrared absorption spectrum of mangiferin as a potassium bromide disk is shown in Fig. 1.

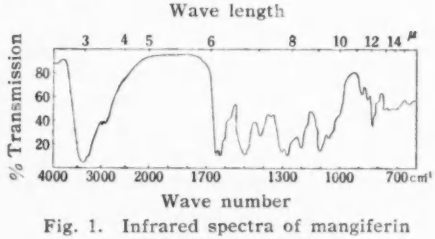


Fig. 1. Infrared spectra of mangiferin (KBr disk method).

The broad absorption around 3338 cm.$^{-1}$ indicates the presence of numerous hydroxyl groups, including those forming intramolecular hydrogen bond. The absorptions at 2932 and 2885 cm.$^{-1}$ indicate the presence of CH_2 in the molecule, but the amount seems to be small judging from its intensity. These absorptions, combined with those at 1490 and 1048 cm.$^{-1}$, suggest the presence of a primary alcoholic group in the molecule. Since there are no absorptions corresponding to CH_3 near 3000, 1450, and 1375cm.$^{-1}$, it can not be considered that the foregoing primary alcoholic group is due to the residual ethanol used for the purification of the pigment. There is no absorption in the region 1650 to 1750 cm.$^{-1}$ and the ester structure of Gorter[5] or the aldehyde structure of Wiechowski[4] can be excluded. The absorption at 1645 cm.$^{-1}$ is the carbonyl band of xanthone nucleus[8] and the sharp absorption at 828 cm.$^{-1}$ (821 cm.$^{-1}$ in Nujol) must be related to the xanthone structure, since it also appears in the spectrum of 1,3,6,7-tetrahydroxyxanthone (825 cm.$^{-1}$, Fig. 2).

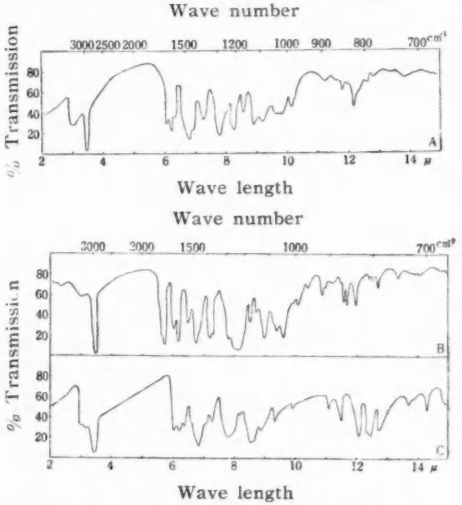


Fig. 2. Infrared spectra (in Nujol) of (A) mangiferin dimethyl ether, (B) mangiferin dimethyl ether acetate, (C) 1,3,6,7-tetrahydroxyxanthone.

According to Barker et al.[9] and Takahashi[10], α-D-glucopyranoside exhibits absorption at 844±8 cm.$^{-1}$ [9] or at 11.6—11.8 μ

7) P. Karrer and M. Pfaehler, *Helv. Chim. Acta*, **17**, 766 (1934).

* When this extraction with ether is omitted, a component that appears above (in ascending paper chromatography) the sugar spot and reduces its R_f, cannot be removed.

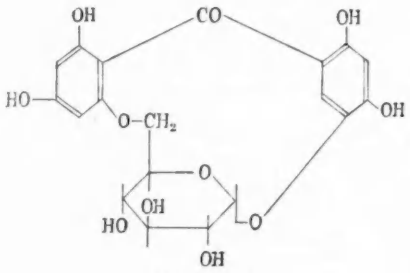
8) S. Kimoto [*J. Pharm. Soc. Japan*, **75**, 763 (1955)] gave 6.07μ (1645cm.$^{-1}$) for xanthone, but E. D. Bergmann and S. Pinchas [*J. chim. phys.*, **49**, 537 (1952); *Chem. Abstr.*, **47**, 3132 (1953)] gave 1658 cm.$^{-1}$. The following values (in Nujol) were obtained: 1,3,6,7-Tetrahydroxyxanthone (1640 cm.$^{-1}$), 1,3,6,7-tetra-acetoxyxanthone (1660 cm.$^{-1}$), 1-hydroxy-3,6,7-trimethoxyxanthone (1665 cm.$^{-1}$).

9) S. A. Barker, E. J. Bourne, M. Stacey and D. H. Whiffen, *J. Chem. Soc.*, **1954**, 171.

10) M. Takahashi, *J. Pharm. Soc. Japan*, **74**, 320 (1954); **75**, 237 (1955).

(862—848 cm.$^{-1}$)[10], irrespective of whether the compound is in the form of glycoside or its derivatives, such as methyl ether. Mangiferin exhibits an absorption at 844 cm.$^{-1}$ and its dimethyl ether and dimethyl ether acetate (Fig. 2) exhibit at 853 cm.$^{-1}$ (in Nujol), but such an absorption is not found in 1,3,6,7-tetrahydroxyxanthone. It follows that the absorption at 844 cm.$^{-1}$ in mangiferin must correspond to that of α-D-glucopyranoside.

The molecular structure shown in (I) may be proposed for mangiferin. Such a structure can be constructed on a molecular model, but this would hardly explain the similarity of the ultraviolet absorption spectrum between mangiferin and 1,3,6,7-tetrahydroxyxanthone, as shown in Part IV. Neither would it explain the formation of only a dimethyl ether with diazomethane. If two hydroxyls are present in the position *peri* to the carbonyl, one could easily be methylated[11].



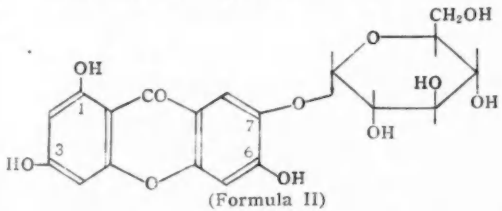
(Formula I)

From the foregoing results, it must be concluded that the sugar is bonded in α-glycosidic type to one of the four hydroxyls in 1,3,6,7-tetrahydroxyxanthone skeleton in mangiferin.

Attempted complete methylation of the pigment with dimethyl sulfate and anhydrous potassium carbonate in dry acetone, turned it into a dark brown syrup, which made it impossible to liberate the sugar portion by acid hydrolysis by the usual method. Assumption of the sugar bonding position was made through coloration reactions.

Mangiferin and its dimethyl ether are both positive to the Gibbs' reaction[12] and Liebermann's nitroso reaction[13], showing the presence of a free hydroxyl without a substituent in the *para*-position (i. e. in 1-position). The presence of a free *meta*-diphenol structure in the mangiferin molecule is known by Brauer's phosphomolybdic acid reaction[14], but this color reaction is negative in mangiferin dimethyl ether. Nagai and Hattori's color reaction[15] with chloropentammincobalt-(III) chloride, $[Co(NH_3)_5Cl]Cl_2$ is negative in both the pigment and its dimethyl ether, indicating the absence of an *ortho*- and *para*-diphenol structures in the molecule. Sevilla and DiMenza[16] have reported a color reaction characteristic of *ortho*-diphenol by ammonium metavanadate, but this was not found applicable in the case of 1,3,6,7-tetrahydroxyxanthone.

From the various experimental results described above, the sugar bonding position may be concluded to be in 6- or 7-position. From the biological fact that euxantic acid(1.7-dihydroxyxanthone 7-glucuronide) is excreted in the urine of rabbits and cattle fed with mangiferin, it may be certain that the sugar is bonded in 7- rather than 6-position. The following formula (II) is proposed as the structural formula for mangiferin.



(Formula II)

If mangiferin were to be represented by the foregoing formula (II), it would be necessary that the hydroxyls in 3- and 6-positions be removed to form euxanthic acid in an animal body. This point still requires further study.

Experimental

All melting points are corrected.

Reaction with Periodic Acid — Mangiferin or its dimethyl ether was suspended in 5% sulfuric acid and powdered potassium periodate was added in small portions to it, by which the solution immediately turned reddish brown. This color faded with sodium thiosulfate and distillation yielded crystals of iodine. The amount of the periodate consumed by titration corresponded to 1.3—3.9 moles, failing to give any definite value. The insoluble portion obtained after the periodate oxidation remained a reddish brown amorphous

11) Y. Tanase, *J. Pharm. Soc. Japan*, **61**, 341 (1941).
12) H. D. Gibbs, *J. Biol. Chem.*, **72**, 649 (1927); M. Tomita and S. Uyeo, *J. Pharm. Soc. Japan*, **61**, 449 (1941).
13) C. Liebermann, *Ber.*, **7**, 247, 1098 (1874).
14) K. Brauer, *Chem. Zeitg.*, **50**, 553 (1926).
15) W. Nagai and S. Hattori, *Acta Phytochim.*, **5**, 1 (1930); *J. Chem. Soc. Japan*, **51**, 162 (1930). Cf. ref. 11).
16) J. Sevilla and A. DiMenza, *Rev. asoc. biochim. argentina*, **14**, 17 (1947); *Chem. Abstr.*, **41**, 6172 (1947).

substance and it could not be induced to crystallize. Beilstein's halogen test: positive.

Aqueous solution of 1 g. of potassium periodate was added dropwise into a suspension of 300mg. of mangiferin in 30 cc. of 5 % sulfuric acid, with shaking, and the mixture was allowed to stand for 36 hours at room temperature (30°C) with occasional shaking. The clear supernatant was decanted and submitted to steam distillation. The addition of 1 cc. of 1 % ethanolic solution of dimedone to 30 cc. of the distillate failed to show the formation of a dimedone adduct. The reaction mixture obtained under the same conditions of oxidation, without separation of the supernatant, was treated with 100 cc. of water, and directly distilled in an oil bath to 50 cc. of the distillate (acid reaction). After removal of iodine crystals, 15 drops of 1 % ethanolic solution of dimedone was added. On standing the mixture over night, 12 mg. of colorless needle crystals were obtained. Recrystallization from ethanol afforded crystals melting at 188°C, undepressed on admixture with authentic sample of formaldimedone, m. p. 188°C.

High-pressure Hydrolysis — A mixture of 1.0 g. of mangiferin and 200 cc. of 10 % sulfuric acid was heated for 2 hours at 140°C in an autoclave. The black, insoluble matter that separated out was removed by filtration, the sulfat ion in the filtrate was quantitatively removed with barium hydroxide, and the filtrate concentrated to 50 cc. This solution was passed through the cation and anion exchange resin 'DIA' (product of Mitsubishi Kasei Co.) to effect complete deionization and further concentrated to 1 cc. of a pale yellow liquid.

This liquid was submitted to paper chromatography by the ascending method, using a mixture (4 : 2 : 1) of butanol : acetic acid: water as the developing solvent. A mixed solution of benzidine (1 g.), trichloroacetic acid (20 cc. of 40 %), glacial acetic acid (20 cc.), and 93 % methanol (160 cc.) was used as the coloring reagent.

In this case, the spot of pure glucose appeared at R_f 0.23, while those of the first sample and the sample to which glucose had been added appeared at R_f 0.20, accompanied by a somewhat broad, feathershaped region, above the spot, without any coloration.

This sample was diluted with about 10 volumes of water and extracted with ether for about 30 hours. The ether-soluble portion afforded a minute amount of yellowish green syrupy substance (which reduces the Fehling and ammoniacal silver nitrate solution). The aqueous solution left after ether extraction was again concentrated and submitted to paper chromatography by which the feathery region disappeared and the spots from pure glucose, the first sample, and the sample with added glucose all appeared at the same R_f 0.24. The color of these spots was also of the same tone.

When 1 % sulfuric acid was used instead of 10 % one without alteration in other conditions, a spot also appeared at the same position.

Hydrolyses under the following conditions failed to indicate the presence of a sugar: heating with mere water at 120°C or 140°C for 2 or 4 hours, heating with 1 % or 10 % sulfuric acid at 120°C for 2 or 4 hours, or at 140°C for 4 hours.

Gibbs' Reaction[12] — To 1 cc. of saturated solution of mangiferin or its dimethyl ether in 70 % ethanol, a piece of sodium acetate crystal was added, followed by a few drops of freshly prepared ethanolic solution of 2,6-dichloroquinone chlorimide. Both gave bluish green (positive) coloration, while acetylmangiferin showed pale pinkish violet and 1,3,6,7-tetra-acetoxyxanthone a pale yellow color.

Liebermann's Nitroso Reaction[13] — A pale brown solution, obtained by dissolving sodium nitrite in well-chilled conc. sulfuric acid, was carefully superimposed on the conc. sulfuric acid solution of mangiferin or its dimethyl ether by which a reddish brown ring appeared at the zone of contact.

Brauer's Reaction[14] — To 1 cc. of saturated aqueous solution of the sample, 0.1 cc. of 10 % aqueous solution of phosphomolybdic acid was added (the color here obtained is designated as A). Then 10 % ammonia water was added carefully in drops (color here obtained is designated as B). Mangiferin showed pale yellowish brown in A and blue in B (positive to *meta* diphenol reaction), the blue color disappearing with excess of ammonia. 1,3,6,7-Tetrahydroxyxanthone showed blue color in A and bluish green in B (positive to *ortho*-diphenol reaction), while mangiferin dimethyl ether failed to show any coloration in either A or B.

Color Reaction to Nagai-Hattori's Cobalt Reagent[15] — To 2 cc. of saturated solution of the sample in 70 % ethanol, 5 drops of a saturated solution of the cobalt reagent** in ethanol was added. No color change was observed after 5 hours with mangiferin, its dimethyl ether, 1-hydroxy-3,6,7-trimethoxyxanthone, or in 1,3,6,7-tetra-acetoxyxanthone. When powdered mangiferin was floated on the ethanolic solution, the color changed to brown after 15 hours, although no change occured within 5 hours. In the case of 1,3,6,7-tetrahydroxyxanthone, the color changed to brown immediately, with turbidity.

Sevilla-DiMenza's Reaction — A few drops of 50 % sulfuric acid containing a small amount of ammonium metavanadate was added to 2 cc. of an aqueous solution containing 1—2 mg. of the sample, or a saturated aqueous solution in the case of mangiferin and xanthone compounds. Only pyrogallol out of the compounds listed below gave a positive reaction (wine red coloration) as described in the literature[16].

Compound (position of OH)	Coloration
Resorcinol (1,3)	Slightly reddish yellow.
Hydroquinone (1,4)	ditto.
Pyrogallol (1,2,3)	Wine red—pale reddish brown.
Phloroglucinol (1,3,5)	Almost colorless.

** $[Co(NH_3)_5Cl]Cl_2$

Orcinol (1—CH_3; 3,5)	Dark gray—pale yellow with brown precipitate.
Mangiferin	Slightly reddish yellow, gradually turning pale, and finally pale yellowish brown.
1,3,6,7-Tetrahydroxyxanthone	Pale dusky black with brown precipitate, gradually turning pale, with dark brown precipitate; finally the solution became pale yellowish brown.

Infrared Absorption Spectra—Spectra were measured with the Perkin-Elmer Model 21 infrared spectrophotometer, by the potassium bromide disk method by Mr. Yusaku Ikegami of the Research Institute for Chemistry of Non-Aqueous Solution, Tohoku University, and by the Nujol method by Mr. Hirotaka Kozuma of the Technical Department, Shin Nippon Chisso Hiyro Co. Minamata.

The writer expresses his gratitude to those who supplied infrared data, to Assistant Professor Kazuyoshi Yagishita and Mr. Naoshi Toya of this laboratory for cooperation in part of the experiments, and to Mr. Chikashi Adachi, President of the Kumamoto Agricultural High School, for permission to use the autoclave.

Department of Chemistry
Kumamoto Women's
University, Kumamoto

Ionization Potentials of Some Organic Molecules. V. Heterocyclic Compounds Containing Nitrogen

By Itiro OMURA, Hiroaki BABA, Keniti HIGASI and Yuichi KANAOKA

(Received April 10, 1957)

What kind of electron is actually responsible for the first ionization potential of a heterocyclic compound containing a nitrogen atom or nitrogen atoms? There are two contradicting views on the problem. One is to ascribe the most loosely bound electron to one of the non-bonding electrons belonging to the N atom, while the other regards one of the π-electrons of the conjugated system most easy to be removed[1]. In previous reports[2] dealing with ionization potentials of pyridine and picolines, the present writers tried to interpret the results of their measurement from the former viewpoint.

As a continuation of the study on ionization potentials, measurements were conducted on three isomers of diazines, three isomers of lutidines and *s*-triazine in the hope that they would provide a fresh clue to knowledge on this point. The results of the measurements on these seven heterocyclic compounds will be fully described in the present article with the possible interpretations.

Experimental Materials

Pyridazine.—3,6-Dichloropyridazine prepared by the chlorination of 3,6-pyridazinediol was hydrogenated in ammonia-ethanol solution with palladium-charcoal at atmospheric pressure. The filtered solution was made alkaline with potassium hydroxide, extracted with ether, dried with potassium carbonate, evaporated and distilled. B.p. 84–86°C (at 14 mm) (Mizzori and Spoerri[3] give b.p. 86–87°C/14 mm).

Pyrimidine.—3,4-Dichloropyrimidine, obtained by the chlorination of uracil, was hydrogenated as in the case of pyridazine to give pyrimidine. Pyrimidine mercurichloride was precipitated from the filtered solution, and distilled with sodium sulphide (nonahydrate). The aqueous distillate was saturated with potassium hydroxide. The separating pyrimidine layer was extracted with ether, dried with potassium hydroxide, evaporated and fractionated to give pyrimidine. B.p. 123°C (Hilbert and Johnson[4] give b.p. 124°C/758 mm).

Pyrazine.—Pyrazine-2,3-dicarboxylic acid (kindly provided by Sankyo Pharm. Co., Ltd.) was decarboxylated in acetic acid solution, made alkaline with sodium hydroxide and steam-distilled[5]. Pyrazine was purified through mercurichloride as in the case of pyrimidine. B.p.

1) C. Reid and R. S. Mulliken, *J. Am. Chem. Soc.*, **76**, 3869 (1954).
2) K. Higasi, I. Omura and H. Baba, *J. Chem. Phys.*, **24**, 623 (1956); H. Baba, I. Omura and K. Higasi, This Bulletin, **29**, 521 (1956).
3) R. H. Mizzori and P. E. Spoerri, *J. Am. Chem. Soc.*, **73**, 1873 (1951).
4) G. E. Hilbert and T. B. Johnson, ibid., **52**, 1152 (1930).
5) S. Gabriel und A. Sonn, *Ber.*, **40**, 4852 (1907).

113°C; m.p. 53-54°C (from ether) (Wolff[6] gives m.p. 55°C).

s-Triazine.—*s*-Triazine was prepared by Grundmann's method[7] from formamidine[8] and sodium diformamide. M.p. 81-82°C (purified by sublimation). (Grundmann[7] gives m.p. 85°C).

Three isomers of lutidines were obtained from Kwanto Chem. Co., Inc., Tokyo. They were distilled before use. 2,3-*Lutidine*, b.p. 161°C. 2,4-*Lutidine*, 157.5-157.8°C. 2,6-*Lutidine*, b.p. 142.2°C. All the temperatures recorded here were uncalibrated.

Experimental Method and Result

The measurement of the first appearance potentials was made by the use of the apparatus described in a previous report[9]. Regarding the evaluation of the ionization potentials, a modified critical slope method was employed. The ionization efficiency curves were plotted on a semilog scale. The pressure of the reference gas, argon, was adjusted so that the initial portions of the curves for the sample and reference gases became nearly parallel to each other. The distance between the two curves along the voltage axis was taken to be the difference between the ionization potentials of the sample and the reference gase*.

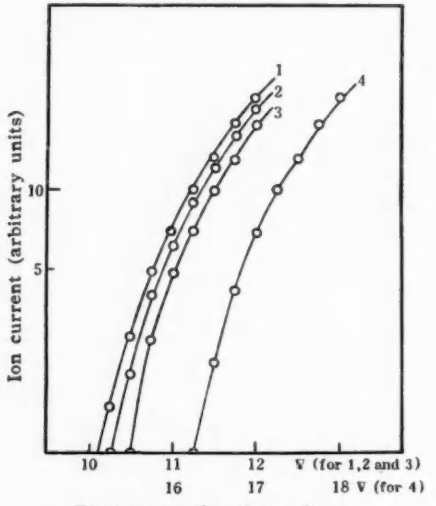


Fig. 1. Relative ionization efficiency curves. 1, pyridazine; 2, pyrimidine; 3, pyrazine; 4, argon.

In Fig. 1 some representative ionization efficiency curves are shown. For *s*-triazine the linear extrapolation method was also used for the sake of comparison.

In a previous report[9] the question was considered as to whether or not the choice of argon as the standard gas is suitable. For the samples treated so far, its use was justified. On account of the following facts the decision then reached is not ultimate nor fully acceptable. The energy spread of emitting electrons is greatly affected by the filament temperature, i.e., about 1800°K in this experiment. Further, the effect of contact potentials contributes to this spread of the energy. As a result the energy difference 0.18 eV between the doublet states, $^2P_{1/2}$ and $^2P_{3/2}$ of argon ion[14] becomes much smaller in comparison with the energy spread of the bombarding electrons used in this sort of experiment*.

In benzene there appears to exist an energy level just under the highest occupied level, the energy separation being only 0.5 eV. It is pointed out by Morrison[15] that the existence of this level becomes a dominant cause of error in the apparent ionization potentials of benzenoid molecules when measured by the ordinary electron impact method. Consequently, if diazines or lutidines are not lacking in respect to such a neighboring level or levels, the measured first potentials of this experiment will correspond to some average values of the first, second and other ionization energies.

The remaining implications come from the space charge effects[16]. With a view to eliminate

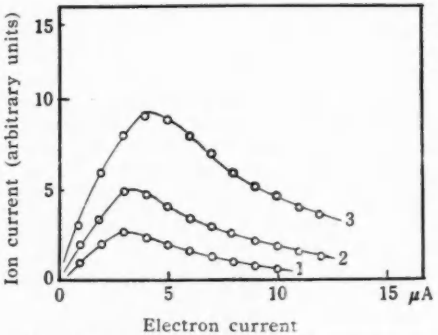


Fig. 2. Dependence of positive ion current (pyridazine) upon electron-beam current. Electron accelerating voltage: 1, 11eV; 2, 12eV; 3, 13eV.

6) L. Wolff, ibid., **26**, 723 (1893).
7) C. Grundmann, H. Schröder und W. Ruske, ibid., **87**, 1866 (1954).
8) D. J. Brown, *J. Appl. Chem.*, **2**, 202 (1952).
9) I. Omura, K. Higasi and H. Baba, This Bulletin, **29**, 501 (1956).
* This procedure has actually been adopted in the work of the previous papers[2,9]. It is a modified application of Honig's method[10], and is essentially the same as employed by Dibeler et al.[11], Lossing et al.[12] and others[13].

10) R. E. Honig, *J. Chem. Phys.*, **16**, 105 (1948).
11) V. H. Dibeler, R. M. Reese and F. L. Mohler, *J. Chem. Phys.*, **20**, 761 (1952).
12) F. P. Lossing, A. W. Tickner and W. A. Bryce, *J. Chem. Phys.*, **19**, 1254 (1951).
13) A. Jacobson, J. Steigman, R. A. Strakna and S. S. Friedland, *J. Chem. Phys.*, **24**, 637 (1956); R. W. Law and J. L. Margrave, *J. Chem. Phys.*, **25**, 1086 (1956).
14) T. Mariner and W. Bleakney, *Phys. Rev.*, **72**, 807 (1947).
15) J. D. Morrison, *J. Chem. Phys.*, **22**, 1219 (1954).
16) J. Marriott and J. D. Craggs, "Applied Mass Spectrometry", London (1954), p. 173.

these effects as nearly as possible, the variation of ion currents with electron currents was closely examined (See Fig. 2). From the curves shown in Fig. 2 such an intensity of electron currents was chosen as to give a maximum intensity of ion currents.

The results of the measurement are collected in Table I. No data for comparison appear to exist in the literature[17].

TABLE I
IONIZATION POTENTIALS OF THE HETEROCYCLIC COMPOUNDS, eV.

Substance	Potentials
Pyridazine	9.86±0.05
Pyrimidine	9.91±0.05
Pyrazine	10.01±0.02
s-Triazine	10.07±0.05 (10.10±0.02)
2,6-Lutidine	9.57±0.02
2,3-Lutidine	9.68±0.02
2,4-Lutidine	9.43±0.02

The value in parenthesis was obtained by the linear extrapolation method, while all others refer to a modified critical slope method, argon being used as the standard gas.

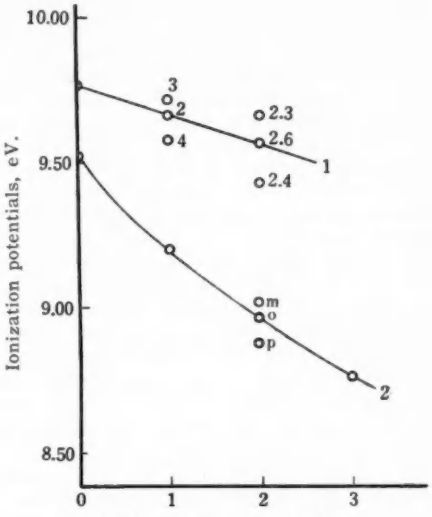


Fig. 3. Ionization potential and methyl substitution. 1, pyridine derivatives; 2, benzene derivatives.

Discussion

Lutidines.—In previous reports[2] dealing with the ionization potentials of xylenes and picolines it was found that the lowering in the potential by methyl substitution was less pronounced in pyridine than in benzene. From this observation it was suggested that the first ionization potentials of pyridine derivatives are largely determined by non-bonding electrons of the N atom, while those of benzene derivatives are determined by π-electrons.

In lutidines two hydrogen atoms of a pyridine molecule are replaced by methyl groups, while in picolines one hydrogen atom is replaced by a methyl group. In all these molecules methyl substitutions always result in the lowering in the potential, but they are not so large as in benzene derivatives. This trend will be clear upon a comparison of the two curves, 1 and 2, in Fig. 3. The ionization potentials obtained for three isomers of lutidines are thus in good accord with the view of the previous papers[2].

Diazines and Triazine.—In previous studies[2] it was found that the replacement of a C-H group of a benzenoid molecule by an N atom always elevates the appearance potential. What would happen, if two or three C-H groups were replaced by the corresponding number of N atoms? The answer will be as follows. If the appearance potential is actually due to non-bonding electrons of the N atom, it will be affected by such a replacement in even the slightest degree. On the contrary, if π-electrons are responsible for the appearance potential, the magnitude of

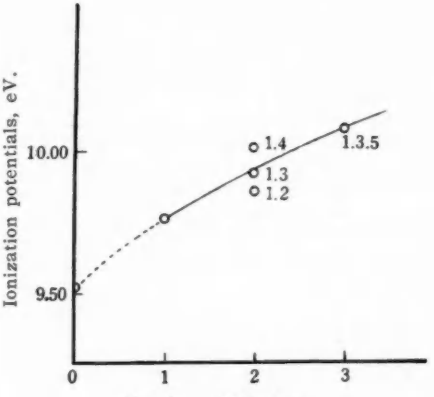


Fig. 4. The effect upon ionization potential of replacement of a C-H group by one or more N atoms.

* The energy spread has not been accurately determined. But refer, for example, to R. H. Vought, *Phys. Rev.*, **71**, 93 (1947).

17) Tables of Ionization Potentials of Molecules and Radicals, *Monogr. Res. Inst. Appl. Elec.*, Hokkaido University, **4**, (1954—7), appendix.

the change will be much greater. Probably its magnitude will be almost the same as in the change when a C–H group in benzene is replaced by one N atom.

With this expectation in mind, the present experiment on diazines and triazine was carried out. The results obtained are shown as a graph in Fig. 4. A smooth curve is obtained when the ionization potentials are plotted against the number of N atoms replaced.

To begin with, it would be better to leave the first view of non-bonding electrons out of consideration, and see if the second view of π-electrons can satisfactorily account for the data on potentials. Fortunately, there are available calculations on π-electron energies for pyridine and diazines[18]. In Table II the energy

TABLE II
IONIZATION POTENTIALS (I), π-ELECTRON DENSITY (q) AND ENERGY OF THE HIGHEST OCCUPIED LEVEL (ε_m)

	I (eV)	ΔI_{obs} (eV)	ε_m (β)	ΔI_π (eV)	q_N	ΔI_n (eV)
	9.76	—	1.051	—	1.29	—
	9.86	0.10	1.305	0.70	1.24	0.14
	9.91	0.15	1.209	0.43	1.28	0.03
	10.01	0.25	1.100	0.13	1.23	0.17

of the highest occupied level, ε_m in β unit*, is shown for each of these compounds. By the use of these values and the assumption $\beta = -2.75$ eV**, the differences in ionization potential between diazines and pyridine can be calculated. (See the values denoted by ΔI_π in Table II). It will be seen that the theoretical differences for 1,2- and 1,3-diazines are much greater than those observed. Contrary to this, the theoretical consideration gives the least change for 1,4-diazine, while the actual observation gives the greatest change.

Next, let the problem be considered from the viewpoint of non-bonding electrons. Against the anticipation based upon this view, diazines were found to have larger ionization potentials than pyridine. But this might be a matter of natural consequence, if the N atoms in diazines have much smaller electron densities than the N atom in pyridine.

The interaction between the N atoms in diazines and a triazine may be better understood, when the electron transmission is grouped into those of π-electrons and σ-electrons. As is evident from the molecular orbital calculation[18], π-electron densities on the N atoms of diazines become smaller than that in pyridine. The decrease is marked at 1,2- and 1,4-positions (Compare the values of q_N in Table II). The decrease in density of σ-electron is also expected in diazines, the order of decrease being 1,2>1,3>1,4. Total electron densities of N atoms in diazines are thus smaller than that of pyridine. Consequently, the effective electronegativities of N atoms increase upon replacement by the N atom.

It will be evident from the above argument that, as far as a qualitative explanation is concerned, the increase in the ionization potentials in diazines and a triazine can be accounted for on the assumption of non-bonding electrons. As the next step, one must make a trial to see whether or not quantitative interpretation is possible on the same basis. In the last column of Table II the results of such a trial are summarized. Indeed, the calculated difference of the ionization potential ΔI_n is in better accord with the observed values than ΔI_π.

The principle of the calculation is as follows. The energy change of the π-electron system δE is expressed by

$$\delta E = \frac{\partial E}{\partial \alpha_r}\delta\alpha_r + \cdots\cdots \simeq q_r \delta\alpha_r, \qquad (1)$$

where $\delta\alpha_r$ is the change of coulomb integral α_r of an atom r and q_r denotes the π-electron density of the atom r[19]. Attention is focussed on the N atom, so that its charge q_N and α_N are considered.

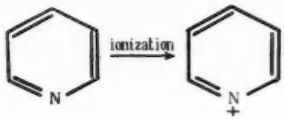
The first ionization may be illustrated as follows.

18) L. E. Orgel, T. L. Cottrell, W. Dick and L. E. Sutton, *Trans. Faraday Soc.*, **47**, 113 (1951).

* The energy ε_m is measured relative to the coulomb integral for a carbon atom. β is defined as the resonance integral of a carbon-carbon bond.

** The value of transition energy to the first excited state for benzene, -2β, derived from the LCAO MO method (neglecting overlap integral), was put as equal to the observed 5.5 eV (C. C. J. Roothaan and R. S. Mulliken, *J. Chem. Phys.*, **16**, 118 (1948)).

19) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.*, **A191**, 39 (1947); **A192**, 16 (1947).



When one non-bonding electron is taken from the N atom, it is supposed that the unit positive charge is localized at the N atom: that is, N^+ is produced. The total energy change of π-electrons on ionization will be approximated by

$$\delta E = q_N \delta\alpha_N \tag{2}$$

where

$$\delta\alpha_N = \alpha_{N^+} - \alpha_N \tag{3}$$

and

$$0 > \alpha_N > \alpha_{N^+} \tag{4}$$

As a further approximation[18] one may put $\delta\alpha_N = \beta^*$ and $\beta = -2.75$ eV. The calculation for δE can be immediately made**, when use is made of q_N values of diazines of Table II.

The value δE thus obtained constitutes only a small fraction of the total energy change in the ionization process. The main part of the ionization energy is of course the energy for removing one electron from a molecule to infinity. But the latter energy is regarded as the same for both pyridine and diazines. By use of this approximation the difference in the ionization potentials between each of the diazines and pyridine may immediately be calculated from the difference in δE. (See ΔI_n in Table II).

In view of the assumptions involved, no strong claim will be made for the reliability of the calculated values ΔI_n. But it appears certain that interaction between N atoms can not be neglected safely and that the present results of these experiments and considerations on diazines and triazine do not contradict the writers' view which favors non-bonding electrons.

Lastly a few words must be added on the accuracy of ordinary electron-bombardment values at large. The ionization potential of benzene, 9.52 eV, obtained by electron bombardment[20] is greater by 0.3 eV than 9.24 eV which is given by both spectroscopic[21] and photoionization method[22]. For pyridine there are available two electron-bombardment values, 9.80 eV[23] and 9.76 eV[2], while photoionization gives a much lower value 9.23 eV[24]. The discrepancy among these values seems to indicate that in pyridine there exists a neighboring level or levels near the highest occupied level.

Under these circumstances one is not absolutely sure as to the accuracy of the values obtained in this sort of measurement. Emphasis in this article has been placed on the general effects of replacement upon the ionization potentials, but not on the fine differences among three isomers. The latter problem is in fact of great importance in chemistry, but at the present stage of research any detailed discussion on this point might be somewhat speculative.

Summary

First ionization potentials of the following substances were determined by a modified critical slope method. Pyridazine 9.86±0.05, pyrimidine 9.91±0.05, pyrazine 10.01±0.02, *s*-triazine 10.07±0.05, 2,3-lutidine 9.68±0.02, 2,4-lutidine 9.43±0.02, and 2,6-lutidine 9.57±0.02 eV. Interpretations of the results are given from the view-point that the ionization potentials of these compounds are largely determined by the non-bonding electrons at the N atom.

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Research Institute of Applied Electricity and the Pharmaceutical Institute Hokkaido University, Sapporo

* $\alpha(-\overset{|}{N}=)=\alpha+\beta$, $\alpha(-\overset{|}{N^+}=)\simeq\alpha(-\overset{|}{N}-)=\alpha+2\beta$. Regarding the latter see H. H. Jaffé, *J. Am. Chem. Soc.*, **76**, 3527 (1954).

** For diazines one may consider that half the unit positive charge appears at each N atom upon the removal of one non-bonding electron. This will not alter the values of δE, if one assumes that the resulting change in coulomb integral of each N atom is $(1/2)\beta$.

20) J. D. Morrison and A. J. C. Nicholson, *J. Chem. Soc.*, **20**, 1021 (1952).
21) W. C. Price, *J. Chem. Phys.*, **3**, 256, 365, 439 (1954).
22) K. Watanabe, *J. Chem. Phys.*, **24**, 1564 (1954).
23) A. Hustrulid, A. Kusch and J. T. Tate, *Phys. Rev.*, **54**, 1037 (1938).
24) K. Watanabe, Private communication.

Relations among Bond Order, Force Constant and Bond Length for the C—C and the C—N Bond in Conjugated Molecules

By Tosinobu ANNO*, Mitsuo ITO, Ryoichi SHIMADA, Akira SADÔ and Wataru MIZUSHIMA

(Received March 15, 1957)

Introduction

In a recent communication[1], the present authors derived following relation between bond length x and bond order p calculated by molecular orbital (MO) approximation:

$$p = 1 - \frac{D_t a_t}{D_s a_s} \frac{\left[\exp\{-a_t(x-x_t)\} - \exp\{-2a_t(x-x_t)\}\right]^2}{\left[\exp\{-a_s(x-x_s)\} - \exp\{-2a_s(x-x_s)\}\right]} \quad (1)$$

where x_s and x_t are the bond length of pure single and triple bonds, respectively. D denotes the bond strength and a is a constant given by

$$a = \sqrt{\frac{k}{2D}}, \quad (2)$$

where k is the bond-stretching force constant. It has also been shown briefly for C—C and C—N bonds in the previous communication that the order-length relations calculated from Eq. (1) are in good agreement with the empirical ones. On the other hand, several empirical relations between force constant and bond length have been proposed by many workers[2]. Among these Badger's relation[3] is the best known and has been accepted most widely. However, the theoretical relations between these quantities have not been derived.

In the present paper we shall propose a full account of the previous communication and a theoretical equation correlating the force constant with the bond length will be proposed, confining ourselves to C—C and C—N bonds.

For C—C bonds, there exist many accurate experimental values of bond lengths and the force constants on the one hand and the calculated values of bond orders on the other. Moreover, the empirical values of parameters necessary in the theoretical equations are known for these molecules better than for the other types of conjugated molecules. Thus the test of the theoretical equations are most feasible for C—C bonds.

For C—N bonds the single and the triple bonds are familiar in chemistry and the physical natures of these bonds are fairly well known. However, for the C—N double bond we have only a few experimental data. Therefore it may be interesting to be able to infer the nature of the C—N double bond from reasonably established relations among bond orders, force constant and bond length.

Derivation of a General Equation Correlating Bond Order and Bond Length

Although Eq. (1) is useful for explaining the relation between bond order and bond length for C—C and C—N bonds, it involves the pure single and triple bonds as references. For C—C bonds, pure single and triple bonds exist in nature as far as the effects of the hyperconjugation or the configuration interaction are neglected. This is also true for C—N single bond, but the pure C—N triple bond does not exist even in the ordinary sense as far as we stand upon the MO viewpoint. Therefore a more general equation which involves Eq. (1) as a special case will be derived first.

Let us take two bonds A_{ij} and B_{ij} whose mobile orders are p_{Aij} and p_{Bij} ($p_{Aij} > p_{Bij}$), respectively, for each bond i—j in a molecule. Other notations used in the following discussion will be easily understood

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* Chemical Laboratory, General Education Department, Kyushu University, Ootsubo-machi, Fukuoka.

T. Anno is greatly indebted to the Dean of the Faculty of Science of Kyushu University and to Professor S. Imanishi for permitting him to continue his work at that Faculty.

1) T. Anno, M. Ito, R. Shimada, A. Sadô, and W. Mizushima, This Bulletin, **29**, 440 (1956).

2) A brief summary of the empirical equations has been given by (a) C. K. Wu and Chang-Tsing Yang, *J. Phys. Chem.*, **48**, 295 (1944) and (b) G. Herzberg, "Spectra of Diatomic Molecules" (D. van Nostrand Company, Inc., New York, 1950) p. 453f.

3) R. M. Badger, *J. Chem. Phys.*, **2**, 128 (1934); **3**, 710 (1935).

by analogy with those described above. The total bond energy of a molecule can be expressed as follows, taking a suitable energy zero:

$$F=\sum_{i-j}D_{Bij}[1-\exp\{-a_{Bij}(x_{ij}-x_{Bij})\}]^2 +2\sum_{i-j}(p_{ij}-p_{Bij})\beta_{ij} +\sum_{i-j}\left|\left(\frac{q_i\alpha_i}{n_i}-\frac{q_{Bi}\alpha_{Bi}}{n_{Bi}}\right)+\left(\frac{q_j\alpha_j}{n_j}-\frac{q_{Bj}\alpha_{Bj}}{n_{Bj}}\right)\right|, \quad (3)$$

where q denotes charge density. Subscripts i and j represent atoms making ends of the bond i–j, n_i and n_{Bi} being the numbers of bonds[4] which start from atom i in the molecule under consideration and the molecule which contains the reference bond B_{ij}, respectively. α and β are the usual coulomb and resonance integral, respectively[5]. We assume here that the terms due to the charge density can be distributed equally among various bonds[4] which start from the atom referring to the term. Then, the total energy of a particular bond is

$$F_{ij}=D_{Eij}[1-\exp\{-a_{Bij}(x_{ij}-x_{Bij})\}]^2 +2(p_{ij}-p_{Eij})\beta_{ij} +\left(\frac{q_i\alpha_i}{n_i}-\frac{q_{Bi}\alpha_{Bi}}{n_{Bi}}\right)+\left(\frac{q_j\alpha_j}{n_j}-\frac{q_{Bj}\alpha_{Bj}}{n_{Bj}}\right). \quad (4)$$

The energy difference between two bonds whose mobile orders are p_A and p_B and the internuclear distances are equally x is represented by

$$\left(\frac{q_{Ai}\alpha_{Ai}}{n_{Ai}}-\frac{q_{Bi}\alpha_{Bi}}{n_{Bi}}\right)+\left(\frac{q_{Aj}\alpha_{Aj}}{n_{Aj}}-\frac{q_{Bj}\alpha_{Bj}}{n_{Bj}}\right) +2(p_{Aij}-p_{Bij})\beta_{ij} =\text{const.}+D_{Aij}[1-\exp\{-a_{Aij}(x_{ij}-x_{Aij})\}]^2 -D_{Bij}[1-\exp\{-a_{Bij}(x_{ij}-x_{Bij})\}]^2. \quad (5)$$

From the equilibrium condition that $\frac{\partial F}{\partial x_{ij}}=0$ and from Eqs. (3) and (5) the following equation is obtained:

$$p=\frac{p_A-p_B}{1-\frac{D_Aa_A}{D_Ba_B}\left[\frac{\exp\{-a_A(x-x_A)\}-\exp\{-2a_A(x-x_A)\}}{\exp\{-a_B(x-x_B)\}-\exp\{-2a_B(x-x_B)\}}\right]}+p_B. \quad (6)$$

4) These bonds should be restricted to those which participate in the conjugation.

5) It should be noted that β_{ij} is assumed to depend only upon the kinds of atom i and j and the distance between these atoms.

It is clear that Eq. (6) reduces to Eq. (1) when the C—C bonds in ethane and acetylene are taken as standards and the effects of hyperconjugation and configuration interaction are neglected. From the meanings of Eqs. (3), (4) and (5) it is clear that D's and a's (equivalently, D's and k's) must refer to hypothetical change where p's and q's do not change from their values in the reference molecules in equilibrium. Let us consider how to derive these constants from those obtained from the "experiment".

When we consider the reference bond B_{ij} at its equilibrium position, Eq. (4) becomes

$$F(x_{Bij})=0. \quad (7)$$

Let the internuclear distance of the reference bond B_{ij} go to infinity leaving $q_i=q_{Bi}$ and $p_{ij}=p_{Bii}$, Eq. (4) becomes

$$F(\infty)_{\text{hypothetical}}=D_{Bij}. \quad (8)$$

Actually, p_{ij} does not necessarily remain equal to p_{Bii} and $q_i\to m_{Bi}$ (m_{Bi} denotes the number of π-electrons of free atom i in its valence state) when $x_{ij}\to\infty$, so that Eq. (4) becomes

$$F(\infty)_{\text{actual}}=D_{Bij}+\frac{1}{n_{Bi}}(m_{Bi}\alpha^{\infty}_{Bi}-q_{Bi}\alpha_{Bi}) +\frac{1}{n_{Bj}}(m_{Bj}\alpha^{\infty}_{Bj}-q_{Bj}\alpha_{Bj}), \quad (9)$$

considering the fact that $\beta_{ij}\to 0$ when $x_{ij}\to\infty$. α^{∞}_{Bi} and α^{∞}_{Bj} denote the limiting values to which α_{Bi} and α_{Bj} approach when $x_{ij}\to\infty$. It is the difference between the left hand sides of Eqs. (7) and (9) that represents the actual D_{Bij} value (denoted by D'_{Bij}). Thus,

$$D_{Bij}=D'_{Bij}-\frac{1}{n_{Bi}}(m_{Bi}\alpha^{\infty}_{Bi}-q_{Bi}\alpha_{Bi}) -\frac{1}{n_{Bj}}(m_{Bj}\alpha^{\infty}_{Bj}-q_{Bj}\alpha_{Aj}). \quad (10)$$

Similarly,

$$D_{Aij}=D'_{Aij}-\frac{1}{n_{Ai}}(m_{Ai}\alpha^{\infty}_{Ai}-q_{Ai}\alpha_{Ai}) -\frac{1}{n_{Aj}}(m_{Aj}\alpha^{\infty}_{Aj}-q_{Aj}\alpha_{Aj}). \quad (11)$$

Thus, D_{Aij} and D_{Bij} values corresponding to the hypothetical changes described above may be obtained from actual D'_{Aij} and D'_{Bij} values using Eqs. (10) and (11).

Differentiating twice Eq. (3) with respect to x_{ij} and inserting the expressions for

$\frac{\partial \beta_{ij}}{\partial x_{ij}}$ and $\frac{\partial^2 \beta_{ij}}{\partial x_{ij}^2}$ obtained from Eq. (5), it follows that[5a]

$$\begin{aligned}\frac{\partial^2 F}{\partial x^2} &= 2a_B D_B[-a_B \exp\{-a_B(x-x_B)\} \\ &\quad +2a_B \exp\{-2a_B(x-x_B)\}] \\ &+ \frac{2\pi}{(p_A-p_B)^2}[a_A D_A[\exp\{-a_A(x-x_A)\} \\ &\quad -\exp\{-2a_A(x-x_A)\}] \\ &\quad -a_B D_B[\exp\{-a_B(x-x_B)\} \\ &\quad -\exp\{-2a_B(x-x_B)\}]]^2 \\ &+\left(\frac{p-p_B}{p_A-p_B}\right)[2a_A D_A[-a_A \exp\{-a_A(x-x_A)\} \\ &\quad +2a_A \exp\{-2a_A(x-x_A)\}] \\ &\quad -2a_B D_B[-a_B \exp\{-a_B(x-x_B)\} \\ &\quad +2a_B \exp\{-2a_B(x-x_B)\}]], \qquad (12)\end{aligned}$$

where π is the self-polarizability of the bond under consideration. At the equilibrium position of the reference bond B, Eq. (12) becomes

$$\begin{aligned}\left(\frac{\partial^2 F}{\partial x^2}\right)_B &\equiv k'_B = k_B \\ &+ \frac{2\pi_B}{(p_A-p_B)^2}(a_A D_A)^2[\exp\{-a_A(x_B-x_A)\} \\ &-\exp\{-2a_A(x_B-x_A)\}]^2, \qquad (13)\end{aligned}$$

and at the equilibrium position of the reference bond A, it becomes

$$\begin{aligned}\left(\frac{\partial^2 F}{\partial x^2}\right)_A &\equiv k'_A = k_A \\ &+ \frac{2\pi_A}{(p_A-p_B)^2}(a_B D_B)^2[\exp\{-a_B(x_A-x_B)\} \\ &-\exp\{-2a_B(x_A-x_B)\}]^2, \qquad (14)\end{aligned}$$

using Eq. (2). Since D_A and D_B values can be obtained in the above-described manner and a's are expressible with D's and k's through Eq. (2), Eqs. (13) and (14) give k_A and k_B corresponding to the hypothetical change from the actual force constants k'_A and k'_B through the iterative process.

Similarly, if the Hooke-type potential functions are used the following formula for order-length relation can be obtained:

$$x = x_B - \frac{x_B - x_A}{1+\frac{k_B}{k_A}\left(\frac{1-p'}{p'}\right)}, \qquad (15)$$

where $p' = (p-p_B)/(p_A-p_B)$ and k_A and k_B may be obtained using

$$k'_B = k_B + \frac{\pi_B}{2(p_A-p_B)^2}\{k_A(x_B-x_A)\}^2, \qquad (16)$$

and

$$k'_A = k_A + \frac{\pi_A}{2(p_A-p_B)^2}\{k_B(x_B-x_A)\}^2, \qquad (17)$$

from the actual force constants k'_A and k'_B. Equation (15) is the general equation which involves those obtained previously[6-8].

Numerical Values of Parameters

As can be seen in the derivation of Eq. (6), this equation is based upon the Morse-type bond-stretching potential function which contains D's and k's as parameters. These parameters may be obtained from the actual D' and k' values as described previously. Although in diatomic molecules D''s and k''s can be obtained from experimental data, for polyatomic molecules circumstances are somewhat different.

Let us first seek for the appropriate values of k''s. As is well known, the force constants take different values depending upon the assumed force fields. However, from the derivation of Eq. (6), if the interactions among the non-bonded atoms can be neglected, it is clear that the appropriate value of k' to be used must correspond to the bond stretching, the bond angles and bond lengths, except the bond length in question, having to remain the same as in the equilibrium. This is the bond-stretching force constant in the most general quadratic potential function which contains all cross terms. Normal coordinate treatment has been carried out for ethane and acetylene, which will be taken as reference molecules in the following discussion for C—C bonds, taking all or almost all the cross terms into consideration. Thus, the following values for C—C bond force constants were taken:

$k'_B = 4.57$[9] and $k'_A = 15.79 \times 10^5$ dynes/cm.[10]

For C—N bonds, the methylamine and

5a) In Eq. (12) subscripts i and j are omitted for brevity.

6) C. A. Coulson, *Proc. Roy. Soc.* (London) **A169**, 413 (1939).
7) T. Anno and A. Sadô, This Bulletin, **28**, 350 (1955).
8) T. Anno and A. Sadô, *J. Chem. Phys.*, **25**, 176 (1956).
9) G. E. Hansen and D. M. Dennison, ibid. **20**, 313 (1952).
10) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules" (D. van Nostrand Co., Inc., New York, 1945), pp. 188—9. This value is the average of the values listed by Herzberg for C_2H_2 and C_2D_2.

hydrogen cyanide molecules may be taken as the reference molecules. While the normal coordinate treatment including the cross terms for the latter molecule gives $k'_A = 18.58 \times 10^5$ dynes/cm.[11], the C—N force constant of the methylamine is not found in the literature. We took the C—N force constant 4.68×10^5 dynes/cm. of the trimethylamine molecule[12] instead.

The most serious difficulty in applying Eq. (6) is concerned with the value of D'. The necessary value of D' must be the energy needed in the process of the rupture of the bond, leaving the other bond lengths or the bond angles unchanged. Thus, the so-called bond-dissociation energy values are not to be used, since the actual dissociation process involves the reorganization of the dissociation products. The adequate value of D' is the bond energy if the "near-atom-effect", in the sense of Glockler[13], can be neglected. As is mentioned previously this type of effect is also neglected in taking the value of k'.

Moreover, in order to calculate the bond energy of the organic compounds from the thermochemical experimental data, it is necessary to know the latent heat of sublimation of carbon (L(C)). Unfortunately, however, the precise value of this quantity is still under discussion[14]. Glockler[15] calculated the bond energies in ethane and acetylene for three conflicting values of L(C). In that paper he recommended L(C) = 169.75 kcal as the best value for this quantity. The bond-energy values calculated by Glockler based on L(C) = 169.75 kcal will be used in the present paper, since L(C) ≈ 170 kcal seems to be the best[16]. The C—C bond energies taken are

$$D'_B = 85.063 \text{ and } D'_A = 182.948 \text{ kcal/mole.}$$

For C—N bonds in methylamine and hydrogen cyanide the calculation of the bond energy requires the dissociation energy of the nitrogen molecule ($D(N_2)$) as well as L(C). The precise value of $D(N_2)$ has also been under discussion[14]. Gaydon[17] has given discussion which supports $D(N_2) = 9.765$ ev, reviewing the previous literatures. Since later works[18–20] seem to support this value of $D(N_2)$, we used this value of $D(N_2)$ in the calculation of the bond energy. Thus the Glockler-type calculation[15,21] yields 64.3 and 201.4 kcal/mole as the C—N bond energies in methylamine and hydrogen cyanide, respectively. Therefore we took

$$D'_B = 64.3 \text{ and } D'_A = 201.4 \text{ kcal/mole.}$$

The C—C or C—N bond lengths in the reference molecules are known with sufficient accuracy. Bond lengths of C—C bonds in ethane[9] and acetylene[22] have been derived from the analyses of rotation-vibration spectra of these molecules. From these we took

$$x_B = 1.543 \text{ and } x_A = 1.207 \text{ Å.}$$

For C—N bonds in methylamine and hydrogen cyanide, recent spectroscopic investigations have given

$$x_B = 1.474^{23} \text{ and } x_A = 1.157 \text{ Å}^{24,25}.$$

Calculation of Bond Order

In order to test the theoretical relation derived above, calculated values of bond orders are necessary. Although for C—C bonds there exist many calculated values of bond order in the literature, the calculated values of C—N bond orders are scarce in the literature, so that calculations of the C—N bond orders have been made for several molecules by MO method using the following assumptions:

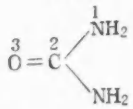
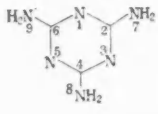
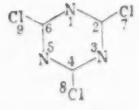
(a) All the resonance integrals between non-adjacent atoms and all the overlap integrals can be neglected.

(b) The ratio of the coulomb integral to the resonance integral in benzene is 4.1; i. e., $\alpha = 4.1\beta$[26].

(c) The coulomb integral of each atom, α_r, is proportional to its electronegativity.

11) A. E. Douglas and D. Sharma, *J. Chem. Phys.*, **21**, 448 (1953).
12) V. H. Siebert, *Z. anorg. allgem. Chem.*, **273**, 161 (1953).
13) G. Glockler, *J. Phys. Chem.*, **56**, 289 (1952).
14) G. Glockler, *Ann. Rev. Phys. Chem.*, **3**, 151 (1952).
15) G. Glockler, *J. Chem. Phys.*, **21**, 1242 (1953).
16) M. Hock, P. E. Blackburn, D. P. Dingledy and H. L. Johnston, *J. Phys. Chem.*, **59**, 97 (1955); W. A. Chupka and M. G. Inghram, ibid., **59**, 100 (1955).
17) A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules". (Dover Publications, Inc., New York, 1950) Chapter IX.
18) J. M. Hendrie, *J. Chem. Phys.*, **22**, 1503 (1954).
19) W. Groth, *Z. physik. Chem.* (Frankfurt), **1**, 300 (1954); *Z. Elektrochem.*, **58**, 752 (1954).
20) D. C. Frost and C. A. McDowell, *Proc. Roy. Soc.* (London), **A236**, 278 (1956).
21) G. Glockler, *J. Chem. Phys.*, **19**, 124 (1951).
22) Reference 10, p. 398.
23) T. Nishikawa, T. Itoh and K. Shimoda, ibid. **23**, 1735 (1955).
24) J. W. Simmons, W. E. Anderson and W. Gordy, *Phys. Rev.*, **77**, 77 (1950).
25) I. R. Dagg and H. W. Thompson, *Trans. Faraday Soc.*, **53**, 455 (1956).
26) C. Sandorfy, *Bull. soc. chim. France*, 615 (1949).

TABLE I

Molecules	r	α_r (β unit)	β_{rs} (β unit)	π-electron densities	Orbital energies (β unit)	
Urea 	1	5.276		1.783	B_1	6.335
			0.757		B_1	5.415
	2	4.346		0.654	A_2	5.276
			0.861		B_1	3.390
	3	5.518		1.780		
Pyridine	1	4.927		1.341	B_2	6.178
			0.839		B_2	5.335
	2	4.180		0.888	A_2	5.131
			0.984		B_2	3.542
	3	4.113		0.982	A_2	3.162
			0.984		B_2	2.322
	4	4.158		0.918		
Pyrazine	1	4.987		1.258	B_{1u}	6.290
			0.859		B_{3g}	5.607
	2	4.192		0.871	B_{2g}	5.158
			0.966		B_{1u}	3.854
	3	4.192		0.871	A_u	3.226
					B_{3g}	2.606
Melamine 	1	4.862		1.433	A''_2	6.557
			0.879		E''	5.914
	2	4.277		0.751	A''_2	5.191
			0.767		E''	5.065
	7	5.260		1.816	E''	3.421
					A''_2	2.652
Cyanuric chloride 	1	4.883		1.404	A''_2	6.502
			0.896		E''	5.737
	2	4.270		0.761	A''_2	5.000
			0.622		E''	4.965
	7	5.010		1.836	E''	3.458
					A''_2	2.658
Hydrogen cyanide $HC\equiv N$ (1 2)	1	4.333		1.347	Π	5.497
			0.876		Π	3.644
	2	4.938		2.653		

The values of the electronegativity used were those listed in Kurita and Kubo[27] for B, C, N and O, while for S and Cl Pauling's values[28] were used.

(d) The resonance integral between adjacent atoms, β_{rs}, is given by $\beta_{rs}=(S_{rs}/S)\beta$[29], where S_{rs} is the overlap integral, which may be evaluated according to Mulliken's Tables[30]. S and β are the overlap and resonance integrals in benzene, respectively.

(e) Inductive effects can be neglected.

(f) α_r and β_{rs} are to be corrected for the formal charge obtained from the calculated electron density according to the way suggested by Nagakura[31,32].

Under the above assumptions the usual MO calculation is repeated until the final results are self-consistent. In the case of the hydrogen cyanide molecule two π-bonds exist, nodal planes of which are perpendicular to each other. These π-bonds will be referred to as π_x and π_y bonds, z direction being taken along the line connecting

27) Y. Kurita and M. Kubo, This Bulletin, **24**, 13(1951).
28) L. Pauling, "The Nature of the Chemical Bond", Cornell University Press, Ithaca, New York, (1940) p. 64.
29) G. W. Wheland, *J. Am. Chem. Soc.*, **64**, 900 (1942).
30) R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).
31) S. Nagakura, This Bulletin, **25**, 164 (1952).
32) S. Nagakura and T. Hosoya, ibid. **25**, 179 (1952).

TABLE II

THE CALCULATED VALUES OF BOND ORDER AND THE EXPERIMENTAL VALUES OF BOND LENGTH FOR SOME C—N BONDS

Molecules	Mobile bond orders		Bond lengths* (in Å)	
	Present calc.	Other methods		
Pyrrole	0.41[b]	0.45[d] 0.50[e]	1.385±0.015	M. W.[h]
Urea	0.540		1.37	X.[i]
Pyridine	0.620	0.534[d,f] 0.64[e] 0.652[g]	1.35	M. W.[j]
Pyrazine	0.639	0.63[e] 0.660[g]	1.35±0.02	E. D.[k]
Melamine C—N (ring) C—N (outer)	 0.474 0.749	 0.449[a] 0.576[a]	 1.37±0.03 1.34±0.01	 E. D.[a]
Cyanuric chloride	0.584	0.622[a]	1.33±0.02	E. D.[a]
Amide group	0.660[c]		1.32±0.02	E. D.[l]
Hydrogen cyanide	1.890		1.157	M. W.[m]

* E. D.: Electron diffraction. X.: X-ray. M. W.: Microwave.

a) Y. Akimoto, This Bulletin, **28**, 1 (1955).
b) S. Nagakura and T. Hosoya, This Bulletin, **25**, 179 (1952). The method of calculation is the same as that used in the present paper, but slightly different values of electronegativity are used.
c) S. Nagakura, This Bulletin, **25**, 164 (1952). The value of bond order listed in this table is calculated using the final values of α's and β's listed in this paper.
d) H. C. Longuet-Higgins and C. A. Coulson, *Trans. Faraday Soc.*, **43**, 87 (1947).
e) L. E. Orgel, T. L. Cottrell, W. Dick and L. E. Sutton, *Trans. Faraday Soc.*, **47**, 113 (1951).
f) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.* (London), **A193**, 447 (1948).
g) D. W. Davies, *Trans. Faraday Soc.*, **51**, 449 (1955).
h) B. Bak, D. Christensen, L. Hansen and J. Rastrup-Andersen, *J. Chem. Phys.*, **24**, 720 (1956).
i) R. W. G. Wyckoff and R. B. Corey, *Z. Krist.*, **89**, 462 (1934).
j) K. E. McCuloh and G. F. Pollow, *J. Chem. Phys.*, **22**, 681 (1954).
k) V. Schomaker and L. Pauling, *J. Am. Chem. Soc.*, **61**, 1769 (1937).
l) R. B. Corey and J. Donohue, *J. Am. Chem. Soc.*, **72**, 2899 (1950).
m) reference 24.

the nuclei. For this molecule the self-consistent result is not to be obtained if the formal charges resulting from both the π_x and π_y bonds are taken into account in the next cycle of calculation concerning π_x or π_y bonds. However, if only the formal charges resulting from the π_x bond are taken into account in the next cycle of calculation concerning the same π_x bond, the self-consistent results are obtained. The same is true also for π_y bond. Therefore calculation of the hydrogen cyanide molecule was made using the additional assumption: only the formal charge resulting from π_x (or π_y) bond should be taken into account for the second cycle of calculation for π_x (or π_y) bond. The final values of α_r, β_{rs} and orbital energies are listed in Table I. Table II contains the bond orders calculated using these parameters. Bond orders calculated with other methods by several workers are also given in Table II.

Bond Order-Bond Length Relation: Test of the Theory

C—C Bonds. — In applying Eq. (6) to C—C bonds, numerical values of parameter derived directly from experiments which have been discussed in a previous section may be used when we use C—C bonds in the ethane and the acetylene molecules as standards and the effects of the hyperconjugation and the configuration interaction are neglected. Fig. 1 contains the theoretical curve thus obtained. In this figure the calculated values of bond order found in the literature for some C—C bonds are also plotted against the experimental values of bond lengths.

It can be seen that the theoretical curve explains fairly well the empirical trend. Deviation of the empirical points from the theoretical curve may be avoided if we take into account the hybridization of the carbon σ-atomic orbital in the same manner as that used by Coulson[33].

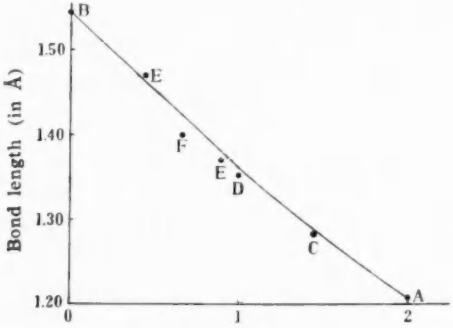


Fig. 1. The relation between bond order and bond length for C—C bonds.
A, Acetylene (a, b)*; B, Ethane (c, b); C, Butatriene (d, e); D, Ethylene (f, b); E, Butadiene (g, b); F, Benzene (g, b).
* (a, b) for example denotes that the bond length and bond order of the acetylene are taken from references a and b, respectively, cited below.
a) reference 22.
b) reference 6.
c) reference 9.
d) B. P. Soicheff, Symposium on Molecular Structure and Spectroscopy, Ohio State University, June 1956.
e) H. C. Longuet-Higgins and F. H. Burkitt, *Trans. Faraday Soc.*, **48**, 1077 (1952).
f) W. S. Gallaway and E. F. Barker, *J. Chem. Phys.*, **10**, 88 (1942).
g) P. W. Allen and L. E. Sutton, *Acta Cryst.*, **3**, 46 (1950).

33) C. A. Coulson, *J. Phys. Chem.*, **56**, 311 (1952).

C—N Bonds. — For C—N bonds, bond energies and force constants of the reference molecules obtained in a previous section should be corrected as described above. If we use the C—N bonds in methylamine and hydrogen cyanide as standards and make the usual approximation, the π-electron densities (q_C, q_N), α_C, α^{∞}_C, α_N and α^{∞}_N, the self-polarizability ($\pi_{CN,CN}$), and the bond order (p_{CN}) of the C—N bond in the hydrogen cyanide molecule are sufficient to make this correction.

Using the assumptions described above it follows that

$$\left.\begin{aligned} &q_C=1.3472,\ q_N=2.6528,\\ &\quad\text{in electron unit,}\\ &\pi_{CN,CN}=0.2300/\beta \end{aligned}\right\} \quad (18)$$

and $p_{CN}=1.890$,

where β is the resonance integral of the C—C bond in benzene the value of which is determined to be 23,000 cm.$^{-1}$ by Platt[34]. The numerical values in (18) are based on

$$\alpha_C=4.33\beta \quad \text{and} \quad \alpha_N=4.94\beta.$$

On the other hand it may be considered that

$$\alpha^{\infty}_C=4.1\beta \quad \text{and} \quad \alpha^{\infty}_N=5.17\beta,$$

from the assumptions on which the MO calculation is based. Therefore, from Eqs. (10), (11), (13) and (14) and using D'_A, D'_B, k'_A, k'_B, x_A and x_B, the values of D_A, D_B, k_A and k_B can be obtained as follows:

$$\left.\begin{aligned} &D_A=175.5\ \text{kcal/mole}\\ &D_B=\ 64.3\ \text{kcal/mole}\\ &k_A=\ 20.01\times10^5\ \text{dynes/cm.}\\ &k_B=\ 4.68\times10^5\ \text{dynes/cm.} \end{aligned}\right\} \quad (19)$$

It is to be noted in the present case that in Eq. (10)

$$m_{Bi}=m_{Bj}=q_{Bi}=q_{Bj}=0,$$

and in Eq. (11)

$$m_{Ai}=m_{Aj}=2, \text{ and } n_{Ai}=n_{Aj}=1.$$

Using the values in (19), Eq. (6) yields a curve shown in Fig. 2.

Plotting the calculated values of bond orders against the experimental data of bond lengths, as is also shown in Fig. 2, it is seen that all the points lie on the theoretical curve within the experimental errors of bond lengths.

Naturally, the numerical value of the bond order is a little affected by the method of calculation as shown in Table

34) J. R. Platt, *J. Chem. Phys.*, **18**, 1168 (1950).

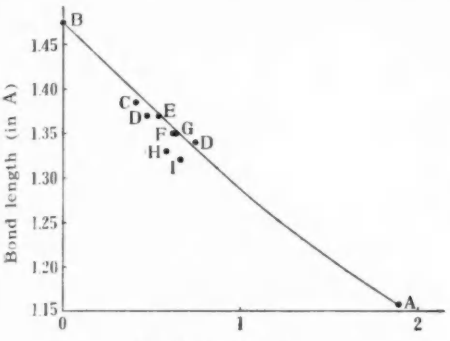


Fig. 2. The relation between bond order and bond length for C—N bonds.
A, Hydrogen cyanide; B, Methylamine; C, Pyrrole; D, Melamine; E, Urea; F, Pyridine; G, Pyrazine; H, Cyanuric chloride; I, Amide group.
In contrast with the corresponding figure in the previous communication (ref. 1) the points for dimeric cyanide are omitted in this figure since the calculation of the bond order of this molecule have been found to be in error.

II. However, the variation is less than 0.10 for most molecules, which may be taken as the measure of reliability of the calculation. According to the theoretical curve, it corresponds to the accuracy of 0.02 Å for bond length, which is nearly the same as the error in the electron-diffraction measurements. We may therefore predict the C—N bond length from the calculated bond order and using the theoretical curve within the experimental errors in the electron diffraction[35].

In concluding this section it is to be noted that the CN "double bond length" can be estimated as follows from the order-length relation obtained above. In the valence bond language the double bond has the "π-bond order" of one half of that of the triple bond which is realized by the CN bond in the hydrogen cyanide molecule if we neglect the homopolar-ionic resonance. Therefore we may consider the "double bond" as a bond whose mobile bond order is one half of that of the CN bond order of the hydrogen cyanide molecule in the molecular orbital language as well. Thus we obtain as the value of mobile bond order of the "double bond" 0.950. This value yields 1.295 Å as the value of "double bond length" from the order-length curve. This is in good agreement with the value of 1.28 Å evaluated as a sum of the covalent radii given by Pauling[36].

Relation between Force Constant and Bond Length

Substituting x, obtainable from Eq. (6), Eq. (12) would give the bond-stretching force constant as a function of p and π and the resulting equation would be analogous to that obtained by Coulson and Longuet-Higgins[37] assuming the Hooke-type potential function. However, since the contribution from the term containing π is relatively unimportant in the right hand side of Eq. (12) we can obtain a relation between force constant and bond length for bonds between a particular pair of atoms if the term containing π is neglected and p is replaced by the right hand side of Eq. (6). The resulting equation is

$$\frac{\partial^2 F}{\partial x^2} \equiv k = k_B g(2g-1) + \frac{k_A h(2h-1) - k_B(2g-1)}{1 - \dfrac{k_A a_B h(1-h)}{k_B a_A g(1-g)}} \tag{20}$$

where $g = \exp\{-a_B(x - x_B)\}$

$h = \exp\{-a_A(x - x_A)\}$,

and use has been made of Eq. (2).

Taking the same molecules as those taken in obtaining order-length relationship as references and using the same value of numerical parameters as used there[38], we obtain a curve showing relation between bond length and force constant for bonds of each pair of atoms. They are full lines in Figs. 3 and 4 for C—C and C—N bond, respectively. Available data of force constants are plotted in the same figures against experimental values of bond lengths. For comparison, curves based on Badger's equation[39] are also drawn in the figures (dotted curves)[39].

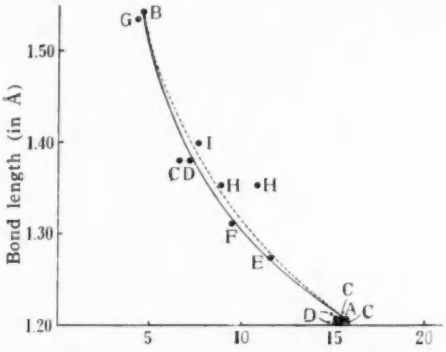
35) Since the CN bond order of the reference HCN molecule and the corrections to D_A and k_A depend upon the assumptions used in the MO calculation, the order-length curve itself depends upon such assumptions. Although this would cause a small additional error in the calculated value of bond length in the region of $p=1\sim2$, it would produce practically no error in the region of $p=0\sim1$ into which the numerical values of the CN bond order of the most interesting molecules fall.

36) Reference 28, p. 164.

37) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.* (London), **A193**, 456 (1948).

38) For k_A of the CN bonds, the uncorrected value was used in order that the curve may pass through the point for the HCN molecule.

39) In drawing the curve based on the Badger's equation the values of parameters in this equation (C and d) were determined from two empirical points for bonds "A" and "B".

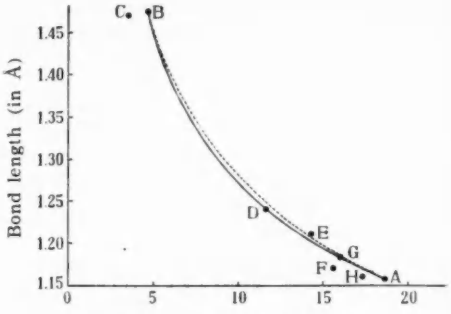


Force constant (in 10^5 dyne/cm.)

Fig. 3. The relation between force constant and bond length for C—C bonds.
A, Acetylene (a, b)*; B, Ethane (c, c); C, Diacetylene (d, e); D, Diacetylene (d, f); E, C_2(c, $^1\Pi_g$) (g, g); F, C_2(X, $^3\Pi_u$) (g, g); G, C_2(B, $^3\Pi_g$) (g, g); H, Ethylene (h, i); I, Benzene (j, k).
* (a, b) for example denotes that the bond length and force constant of the acetylene are taken from references a and b, respectively, cited below.
a) reference 22.
b) reference 10.
c) reference 9.
d) G. D. Graine and H. W. Thompson, *Trans. Faraday Soc.*, **49**, 1273 (1953).
e) S. M. Ferigle, F. F. Cleveland and A. G. Meister, *J. Chem. Phys.*, **20**, 526 (1952).
f) A. V. Jones, *Proc. Roy. Soc.* (London), **A211**, 285 (1952).
g) reference 2b, p. 513.
h) W. S. Gallaway and E. F. Barker, *J. Chem. Phys.*, **10**, 88 (1942).
i) B. L. Crawford, Jr., J. E. Lancaster and R. G. Inskeep, *J. Chem. Phys.*, **21**, 678 (1953).
j) P. W. Allen and L. E. Sutton, *Acta Cryst.*, **3**, 46 (1950).
k) F. M. Garforth, C. K. Ingold and H. G. Poole, *J. Chem. Soc.*, **1948**, 491.

Comparing our theoretical curve with the curve based on Badger's relation, it is seen that both curves coincide fairly well with each other over the whole region of bond length.

It is mentioned in the preceding section that the bond length of the C—N double bond may be predicted to be 1.295 Å from the theoretical orderlength relation. Combining this value with Eq. (20), we can obtain the force constant of the C—N double bond as 9.1×10^5 dynes/cm.



Force constant (in 10^5 dyne/cm.)

Fig. 4. The relation between force constant and bond length for C—N bonds.
A, Hydrogen cyanide (a, b)*; B, Methylamine (c, d); C, Ethylamine (e, f); D, C=N radical (g, g); E, Thiocyanate ion (h, h); F, C≡N radical (g, g); G, Methyl carbylamine (i, h); H, Ethane nitril (e, h).
* (a, b) for example denotes that the bond length and force constant of the hydrogen cyanide are taken from references a and b, respectively, cited below.
a) reference 24.
b) reference 11.
c) reference 23.
d) reference 12. The precise values of force constants of methylamine are not found in the literature, so we assume that the CN force constant in methylamine is equal to that in trimethylamine.
e) Landolt-Börnstein, "Zahlenwerte und Funktionen" (Springer, Berlin, 1951), Vol. I, Part 2, Molekeln I, p. 17.
f) ibid., p. 234.
g) ibid., p. 228.
h) ibid., p. 230.
i) ibid., p. 18.

Summary

A general equation correlating bond orders with bond lengths of bonds between any particular pair of atoms in the conjugated systems are proposed. To test this equation applications have been made for C—C and C—N bonds. Because of the scarcity of the calculated values of bond orders for C—N bonds in the literature, bond orders of several molecules containing C—N bonds have been calculated. It is shown that the order-length relation is in good agreement with experiments. A theoretical, although approximate, equation correlating bond lengths with force constants has also been proposed and applied to C—C and C—N bonds. From these relations the length and the stretching force constant of C—N double bond

are estimated to be 1.295 Å and 9.1×10^5 dynes/cm, respectively, the former being in agreement with the value calculated from the covalent radii given by Pauling.

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Department of Chemistry
Faculty of Science
Kyushu University
Hakozaki, Fukuoka

Spectrochemical Study of Microscopic Crystals. XIV[1]. *Absorption Spectra and Structure of Dibenzene-chromium(I) Iodide*

By Shoichiro YAMADA, Hiroji NAKAMURA and Ryutaro TSUCHIDA

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In the course of these several years, dicyclopentadienylcompounds of various metallic elements were prepared, and their chemical and physical properties were extensively studied from various sides[2]. Recently Fischer and Hafner[3] succeeded in preparing an interesting compound with a molecular formula of $Cr(C_6H_6)_2$, which was shown through an X-ray examination[4] to consist of sandwich molecules resembling the molecule of dicyclopentadienyliron(II), $Fe(C_5H_5)_2$[5]. Preparations also were reported of several other compounds of similar structure[3,6]. Although reports have appeared concerning the properties of the compounds of this type, their electronic states are still open to question.

In order to study the linkages in the compounds of this type, the present authors have determined absorption spectra of dibenzenechromium(I) iodide, $[Cr(C_6H_6)_2]I$, in water and ethyl alcohol, and also in the crystalline state. Description and discussion of the measurements are given below.

Experimental

Material.—Crystals of dibenzene-chromium(I) iodide were kindly donated by Dr. E. O. Fischer of "Technische Hochschule, München". The yellow crystals of the compound show a well-developed prism face of a rectangular form, on which the measurement of dichroism has been made. It has been found in the course of the measurement that the crystal undergoes photodecomposition with ultra-violet light. On the contrary, the crystal is comparatively stable in the dark.

Measurement.—Visible and ultra-violet spectra of the compound in the crystalline state have been measured on the above-mentioned face using Tsuchida-Kobayashi's microscopic method[7] with polarized light having its electric vector along and perpendicular to the direction of elongation. The *c*- and the *a*-absorption refer to absorption with the electric vector along and perpendicular to the direction of elongation, respectively.

Visible and ultra-violet absorption spectra in solution and an infra-red spectrum in pressed potassium bromide have been determined with a Beckman DU spectrophotometer and a Hilger H 800 infra-red spectrophotometer, respectively. The symbols used here are the same as those in the former reports of this series.

Results and Discussion

The results of the present measurements are shown in Fig. 1, Table I, Table II and Table III.

Whereas benzene molecules in solution are known to show a characteristic absorption band at about 2600 Å which involves a distinct fine structure, the present measurement indicates that $[Cr(C_6H_6)_2]I$ shows no absorption band of the above sort. It is supposed, therefore, that the electronic state of the benzene rings

1) Part XIII of this series, S. Yamada and R. Tsuchida, This Bulletin, **29**, 894 (1956).
2) See, for example, E. O. Fischer, *Angew. Chem.*, **67**, 475 (1955).
3) E. O. Fischer and W. Hafner, *Z. Naturforsch.*, **10b**, 665 (1955).
4) E. Weiss and E. O. Fischer, *Z. anorg. allgem. Chem.*, **286**, 142 (1956).
5) E. O. Fischer and W. Pfab, *Z. Naturforsch.*, **7b**, 377 (1952); P. F. Eiland and R. Pepinsky, *J. Am. Chem. Soc.*, **74**, 4971 (1952); J. D. Dunitz and L. E. Orgel, *Nature*, **171**, 121 (1953).
6) H. H. Zeiss and W. Herwig, *J. Am. Chem. Soc.*, **78**, 5959 (1956).
7) R. Tsuchida and M. Kobayashi, "The Colour and the Structure of Metallic Compounds," Zoshindo, Osaka, 1944, p. 180 (in Japanese).

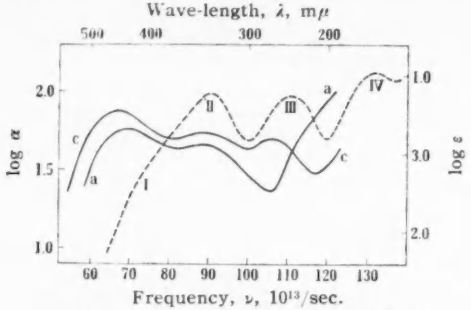

Fig. 1. Absorption spectra of $[Cr(C_6H_6)_2]I$ in the crystalline state (——) and in aqueous solution (·····).

within the chromium(I) compound is quite different from that of a free benzene molecule. Thus it is most likely that the π-electrons on the benzene rings are considerably attracted toward the central chromium ion to form firm linkages with it.

It is generally known that, when a metal ion having an unfilled *d*-electron shell forms a complex group with ligands, a few absorption bands of moderate intensity, rather characteristic of the metal ion, must appear in the visible or near-ultraviolet regions. To this type of absorption bands may belong the band I of the chromium(I) compound in question. When the solvent is alternated with a more polar one, this band is found to undergo only very slight solvent effect, which seems to be in agreement with the above assignment[8].

TABLE I

VISIBLE AND ULTRA-VIOLET ABSORPTION SPECTRA OF $[Cr(C_6H_6)_2]I$ IN CRYSTALLINE STATE AND IN SOLUTION

absorption band	I	II	III	IV
In crystalline state				
ν, 10^{13} sec^{-1}	67.2	86-90	105.6	>120
Δ (log α)	0.12	0.1	0.4	marked
stronger component	Z	Z	Z	X,Y
In H_2O				
ν, 10^{13} sec^{-1}	ca. 76	90	110.6	133.5
log ε	ca. 2.75	3.76	3.75	4.14
In C_2H_5OH				
ν, 10^{13} sec^{-1}	ca. 76	89.8	110.0	139.2
log ε	ca. 2.75	3.80	3.78	4.28
solvent effect	very slight	slight blue shift	slight blue shift	great red shift

The fact that the bands II and III have great intensity in solution suggests that they are different from the type I of absorption bands with much lower intensity. We suppose that these bands may be closely related with the benzene molecules. The bands show a slight but definite "blue shift" when the solvent is changed from a less polar to a more polar one. The "blue shift" indicates that the bands in question correspond to transitions of an n-π type, showing agreement with the above assignment. The bands II and III may not be considered as a band of such a kind that is identical in its origin with the typical absorption bands of free benzene, since the band of free benzene is known to show a "red shift".

The crystal structure of $[Cr(C_6H_6)_2]I$ is not known as yet. Although the exact arrangement of $[Cr(C_6H_6)_2]^+$ ions in the crystal can not be determined, we may be able to estimate the principal features of dichroism for the complex ion itself on a suitable assumption about the arrangement of the complex ions in the crystal. Previous studies on the dichroism of planar metallic complexes[9] indicate that for an absorption band in the longer wave-length of a planar metallic complex, which is closely related with the linkages within the complex, absorption is stronger along the direction in which the linkages exist than along the direction normal to it. Since the band I is assumed to be closely related with the linkage between the chromium ion and the benzene molecules, similar relationships to the above-mentioned should hold for the band I of the chromium(I) compound.

The present dichroism measurement with the crystal indicates that the polarization for the band I is definite, though not very great. Then we may assume that the *c*-absorption in Fig. 1 may represent the main characteristics of the *z*-absorption, the *z*-absorption being absorption with polarized light having its electric vector perpendicular to the benzene rings.

If the linkages between the benzene molecules and a chromium ion were similar to those in aromatic molecular compounds such as the linkage between

8) About the solvent effect upon absorption spectra, see, for example, M. Kasha, *Faraday Soc. Discussion*, No. 9, 14 (1950); H. McConnell, *J. Chem. Phys.*, **20**, 700 (1952); K. Nakamoto, M. Kobayashi and R. Tsuchida, ibid., **22**, 957 (1954).

9) S. Yamada and R. Tsuchida, This Bulletin, **29**, 421 (1956); ibid., **26**, 492 (1953); *J. Am. Chem. Soc.*, **73**, 1182 (1951); *Annual Report of Scient. Works, Fac. Sci. Osaka Univ.*, **4**, 79 (1956), etc.

quinone and hydroquinone molecules in quinhydrone, there should appear on the long wave-length side a new type of absorption band which would be broad and strong, and greatly polarized along the *z*-direction[10]. Since this type of absorption is not observed, the linkage similar to those in aromatic molecular compounds may not be present in the chromium(I) compound.

If aromaticity of the benzene rings in this chromium(I) compound were comparatively marked, the dichroism similar to the benzene rings would be observed, just as in most benzene derivatives. The dichroism of the benzene rings, which was determined with an ordinary type of benzene derivatives, indicates that absorption is more intense along the benzene ring than along the direction normal to it[11]. Since no dichroism of the above sort or a band with a fine structure is observed, the electronic state of the benzene molecules in this chromium(I) compound seems to be far from the state of free benzene molecules. The possibility may still remain that the band with a fine structure would be very weak, being hidden by the bands of much greater intensity. This possibility, however, may be neglected, judging from the general aspect of the absorption curve with the present compound.

The present measurement also indicates that with respect to the band IV absorption is much more intense along the plane of the benzene rings than along the direction normal to the benzene rings. From analogy with the dichroism of the benzene rings[11], it is suggested that the band IV is closely connected with the linkages within the benzene rings.

A marked "red shift" has been observed for the band IV, showing that the band corresponds to a "π-π" transition. The band IV does not correspond to the band at 2600 Å of free benzene, since both the magnitude of the red shift and the intensity seem to be too great, as compared with the values for the band at 2600 Å of free benzene.

Infra-red absorption bands of the chromium(I) compound are shown in Table II and Table III together with corresponding values of related compounds. The chromium(I) compound has an absorption band at 1428 cm.$^{-1}$ for a C–C stretching vibration in the benzene plane. It is seen that the C–C vibration in the chromium(I) compound is displaced from the original position of free benzene to a considerably smaller wave-number, being very close to the corresponding values[12] for dicyclopentadienyl-iron. From mutual comparison of the values in Table III, the electronic state of the benzene rings in $[Cr(C_6H_6)_2]I$ may be concluded to be between the states of ordinary aromatic and aliphatic carbon atoms, and to resemble the state of cyclopentadienyl-radicals in dicyclopentadienyl-iron(II). Thus the benzene rings in the chromium (I) compound may have less aromaticity than free benzene, though they still keep some of their unsaturated character.

Table II

Infra-red absorption bands of $[Cr(C_6H_6)_2]I$ in pressed potassium bromide

freq. cm.$^{-1}$	intensity	freq. cm.$^{-1}$	intensity
795	v. str.	1145	m.
890	w.	1385	w.
974	str.	1428	str.
995, 1005 (double)	m.	3025	m.

Table III

Skeletal C-C vibration

compound	skeletal vibr. cm^{-1}	ref.
$Fe(C_5H_5)_2$	1410	12
$Cr(C_6H_6)_2$	1428	3
$[Cr(C_6H_6)_2]I$	1428	
C_6H_6	1500	a)
C-C double	1600–1680	a)
C-C single	800–1200	a)

a) See, for example, J. L. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen & Co., London, 1954.

Summarizing all the facts as described above, absorption spectra in the infra-red, the visible and the ultra-violet region seems to be understandable on the basis of the following assumption about the electronic state and linkages within the chromium(I) compound in question.

The benzene rings in $[Cr(C_6H_6)_2]I$ have an electronic state which deviates greatly from the state of the ordinary benzene rings, involving very little aromaticity.

10) R. Tsuchida, M. Kobayashi and K. Nakamoto, *Nature*, **167**, 726 (1951); K. Nakamoto, *J. Am. Chem. Soc.*, **74**, 1739 (1952), *etc.*

11) R. Tsuchida, M. Kobayashi and K. Nakamoto, *J. Chem. Soc. Japan*, **70**, 12 (1949); K. Nakamoto, *J. Am. Chem. Soc.*, **74**, 390 (1952); G. Scheibe, S. Hartwig and H. Müller, *Z. Elektrochem.*, **49**, 372 (1943); D. P. Craig and L. E. Lyons, *Nature*, **169**, 1102 (1952), *etc.*

12) L. Kaplan, W. L. Kester and J. Katz, *J. Am. Chem. Soc.*, **74** 5531 (1952); E. R. Lippincott and R. D. Nelson, *J. Chem. Phys.*, **21**, 1307 (1953).

Thus we are inclined to conclude that π-electrons of the benzene rings in $[Cr(C_6H_6)_2]I$ may be strongly attracted so that the electronic state of the benzene rings is far from the state of the ordinary benzene rings and somewhat near the state of the cyclopentadienyl-radicals in dicyclopentadienyl-iron(II)[13].

Summary

Polarized absorption spectra of $[Cr(C_6H_6)_2]I$ in the visible and the ultraviolet region were quantitatively determined by Tsuchida-Kobayashi's microscopic method using a single crystal. Visible and ultraviolet absorption spectra in solution and an infra-red spectrum in potassium bromide disks were also determined.

From the results of the measurements, it was concluded that the electronic state of the benzene rings in $[Cr(C_6H_6)_2]I$ deviates greatly from the state of free benzene and that the π-electrons of the benzene rings are attracted remarkably toward the chromium ion to form firm linkages.

The present authors wish to express heartiest thanks to Dr. E. O. Fischer for a precious sample of dibenzene-chromium (I) iodide. The work reported here was supported in part by a grant in aid from the Ministry of Education.

Department of Chemistry, Faculty of Science, Osaka University
Kita-ku, Osaka

13) S. Yamada, A. Nakahara and R. Tsuchida, *J. Chem. Phys.*, **22**, 1620 (1954); This Bulletin, **28**, 465 (1955).

*Polarography of Bis(nitrophenyl)arsinic Acids**

By Masao MARUYAMA and Toshiko FURUYA

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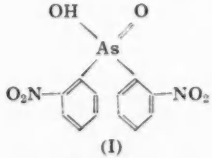
There are numerous reports on the study of polarography of aromatic nitro compounds but those on organic arsenic compounds are comparatively rare, brief reports being made on phenylarsonic acids[1,2], diphenylarsinic oxide, and dephenylarsinic acid[3]. It has been shown that phenylarsonic acids show a reduction wave with a half-wave potential of −1.25 V. vs. N.C.E. in a buffer solution of pH 2.97 but nothing has been given as to its electrolytic reduction mechanism and limiting current value, nor its proportionality with the concentration. As for diphenylarsinic oxide and acid, only brief mention is made of the fact that they show reduction waves and consequently could be utilized for indirect determination of diphenylcyanarsine.

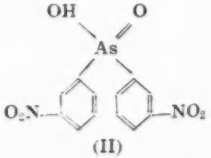
In the present series of experiments, polarographic behavior of bis (nitrophenyl) arsinic acids, including diphenylarsinic acid, was clarified and discussions are made on the results of studies made in order to obtain some fundamental data for its utilization for quantitative determination. Further, a few examples of the determination are described.

Experimental

There are six isomers of bis(nitrophenyl)arsinic acid according to the position of the two nitro groups, viz. 2,2'-(I)' 3,3'-(II), 4,4'-(III), 2,3'-(IV), 2,4'-(V), and 3,4'-(VI). These six isomers and a compound without nitro group, diphenylarsinic acid, (VII), were submitted to the experiments. The melting points of these compounds are indicated with their structures.



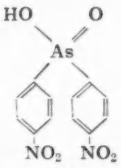
(I)
m.p. 218°C(decomp.)



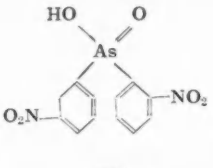
(II)
m.p. 244°C(decomp.)

* The Gist of the present report was presented at the 8th Annual Meeting of the Chemical Society of Japan (April, 1955).

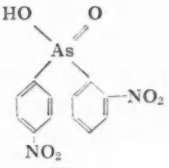
1) B. Breyer, *Ber.*, **71**, 163 (1938).
2) B. Breyer, *Biochem. Z.*, **301**, 65 (1939).
3) M. Suzuki and I. Tachi, *J. Electrochem. Soc. Japan*, **16**, 152 (1948).



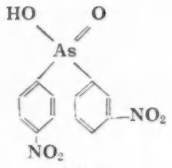
(III)
m.p. 263°C (decomp.)



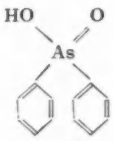
(IV)
m.p. 257°C (decomp.)



(V)
m.p. 248-250°C



(VI)
m.p. 230°C



(VII)
m.p. 167-168°C

The composition of the buffer solutions used is listed below and pH was measured with a glass electrode pH meter (manufactured by the Yamashita Denshiki Kagakukeiki Reserch Laboratory).

pH 1.04 .....0.1 N HCl
pH 2.2-7.0.....McIlvaine
(0.1 M citric acid-0.2 M Na_2HPO_4)
pH 8.0-12.38...Sörensen
(0.1 M KH_2PO_4-0.05 M $Na_2B_4O_7$)
pH 13.05 .....0.1 N NaOH

All the samples were dissolved in distilled water and mixed with the buffer solution to be used as the electrolytic solution. This solution was bubbled with purified nitrogen gas and washed with chromous chloride solution, for about 15 minutes to remove dissolved oxygen.

The apparatus used was a Heyrovsky-Shikata type photo-recording polarograph (Yanagimoto Model 52). The sensitivity of the galvanometer was 1.47×10^{-9} amp./1 mm./m. and the dropping mercury cathode used had a capillary constant of m=2.35 mg./sec., t=4.26 sec./drop.

The polarographic cell used was an H-type with a ground-glass joint (universal) as shown in Fig. 1, which has long been used in this laboratory.

Microelectrolysis was carried out in accordance with the method of Gilbert and Rideal[4]. A definite amount (0.2-0.3 ml.) of the electrolytic solution was electrolyzed at the dropping mercury electrode and the number of electrons, *n*, was calculated from the decrease in wave height in the polarogram before and after the electrolysis,

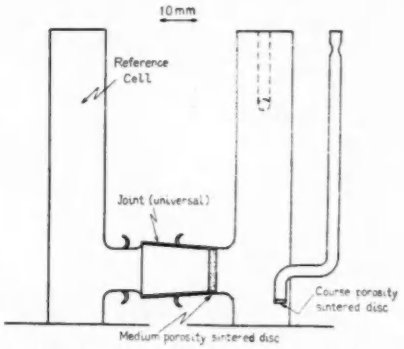


Fig. 1. H-Type-polarographic cell

according to the following equation:

$$\frac{d(\log h)}{dt} = \frac{k_2}{2.30.n.F.v.k_1}$$

All the experiments were carried out in a thermostat maintained at 25°±0.1°C.

Experimental Results and Discussion

(I) Reduction in Buffer Solutions of Various pH Values.—The polarograms of the six isomers of bis(nitrophenyl)arsinic acids in buffer solutions of various pH values show reduction waves of complicated form. Even at the same pH, different isomers show different wave forms, as indicated in Fig. 2, and the wave form changes further with changes in pH.

These complicated reduction waves were classified into two portions, designated as 1st and 2nd waves, and each was examined. The 1st wave that appears initially is composed of one or two steps, the slope is more acute than the 2nd wave, and appears in the whole range of pH 1 to 13. The complicated waves appearing at more negative potentials than the 1st wave are collectively taken as the 2nd wave.

The 1st Wave. The half-wave potential of the 1st wave tends to shift to the negative side as the pH value increases but the wave height remains almost constant for all the isomers and through all pH values. The wave form is a one- or two-step wave below pH 7 but becomes a one-step wave above pH 8 for all six isomers (Table I).

Since this 1st wave does not appear in the reduction wave of diphenylarsinic acid, it is certain that the wave is due to

4) G. A. Gilbert and E. K. Rideal, *Trans. Faraday Soc.*, **47**, 396 (1951).

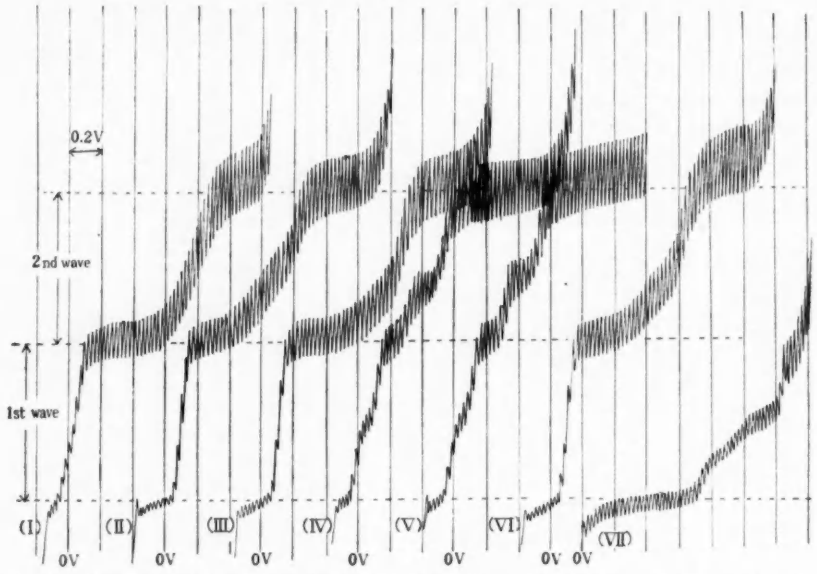


Fig. 2. Typical polarograms of Bis(nitrophenyl)arsinic acids diphenylarsinic acid in buffer solution of pH 2.2.
(I) 2,2′-compound (II) 3,3′-compound (III) 4,4′-compound
(IV) 2,3′-compound (V) 2,4′-compound (VI) 3,4′-compound
(VII) diphenylarsinic acid

TABLE I
HALF-WAVE POTENTIAL OF THE 1ST WAVE OF BIS(NITROPHENYL)ARSINIC ACIDS AT VARIOUS pH VALUES
$\pi_{1/2}$ mV(vs. S. C. E.)

pH	2,2′-*	3,3′-	4,4′-	2,3′-	2,4′-	3,4′-
1.04	−004	−071	−056	+046 −076	+048 −064	−062
2.2	−048	−110	−111	+008 −128	+005 −120	−111
3.0	−064	−152	−146	−030 −171	−035 −160	−152
4.0	−110	−198	−196	−070 −215	−074 −220	−200
5.0	−180	−270	−272	−174 −284	−142 −265	−270
6.0	−281	−355	−340	−243 −352	−246 −348	−338
7.0	−360	−390	−388	−324 −392	−325 −378	−384
8.0	−440	−450	−450	−430	−422	−440
9.0	−500	−494	−490	−490	−480	−492
10.0	−549	−550	−535	−544	−534	−512
11.0	−560	−586	−552	−565	−554	−528
12.38	−630	−652	−630	−650	−620	−628
13.05	−670	−660	−664	−626	−650	−664

* It was difficult to measure the half-wave potential on the acid side as a two-step wave and, therefore, it was obtained as a one-step wave.

the reduction of the nitro group, At below pH 7, the nitro group in the 2-position is reduced in a more positive potential than that in the 3- or 4-position, as was evidenced in the case of pH 2.2 shown in Fig. 2, and this results in two-step waves appearing in the 2,3- and 2,4-compounds, the ratio of wave heights being 1 : 1. The wave of the 2,2′-compounds, when well examined, appears to be a two-step wave and its wave height ratio is 1 : 3. This is assumed to be due to the fact that one of the four oxygen atoms of the two nitro groups forms a hydrogen bond with the hydrogen atom of the hydroxyl group in the molecule, so that this oxygen atom is reduced at more positive potentials than the other three oxygen atoms. But it is necessary to study this matter in detail further. A similar phenomenon was assumed to occur with 2,3′- and 2,4′-compounds but such waves could not be observed in the polarogram.

Analysis of the wave form indicated the 1st wave to be irreversible and its limiting current is controlled by a diffusion process, as will be described later. The number of electrons, n, taking part in the reduction in buffer solutions of pH 2.2–3.0, by microelectrolysis according to the

method of Gilbert and Rideal[4] was approximately 8, n being 7.8 and 7.7 in the 2,2'-compound, 8.1 and 7.7 in the 3,3'-compound, and 8.0 and 7.8 in the 4,4'-compound. From such a fact, it may be assumed that the 1st wave of bis(nitrophenyl)arsinic acids is due to the reduction of the two nitro groups into $-NHOH$.

$$-NO_2 \xrightarrow[-H_2O]{4e+4H^+} -NHOH$$

The 2nd Wave. As shown by the example in Fig. 2, the 2nd wave is composed of complicated wave forms which would be difficult to analyze. The 2nd wave appears only below pH 6 in compounds not possessing $-NO_2$ group in 2-position, the wave disappearing at above pH 7. In the 2,2'-, 2,3'-, and 2,4'-compounds, however, the 2nd wave appears as a complicated wave with a maximum, even at above pH 7 up to pH 10, although the wave height decreases drastically, disappearing at above pH 11. Table II shows the relationship between pH and the 1st and the 2nd wave for all the isomers.

As was mentioned earlier, the half-wave potential of the 2nd wave is difficult to determine, wing to the complicated form of its reduction wave. Moreover, the wave form varies with pH even in one isomer so that it is impossible to compare the half-wave potential of the 2nd wave of each isomer. In each individual isomer,

Table II

Relationship between pH and 1st and 2nd waves in bis(nitrophenyl)arsinic acids

Positions of $-NO_2$	The 1st wave	The 2nd wave
2,2'-	pH 1-7: 2-step wave with wave height 1:3 pH 8-13: 1-step wave	pH 1-10: 2nd wave observed pH 11-13: not apparent
2,3'-	pH 1-7: 2-step wave with wave height 1:1 pH 8-13: 1-step wave	—ditto—
2,4'-	—ditto—	—ditto—
3,3'-	pH 1-13: 1-step wave	pH 1-6: 2nd wave observed pH 7-13: not apparent
3,4'-	—ditto—	—ditto—
4,4'-	—ditto—	—ditto—

Table III

Wave height of 1st and 2nd wave and their ratio of bis(nitrophenyl)arsinic acids

(Sample concentration: 1.14×10^{-4}M/l)

position of $-NO_2$		pH 1.04	pH 2.2	pH 3.0	pH 4.0	pH 5.0	Mean
	1st wave	3.63	3.60	3.71	3.62	···	3.64
2,2'-	2nd wave	3.32	3.35	3.24	2.80	···	3.18
	ratio	8 : 7.3	8 : 7.5	8 : 7.0	8 : 6.2	···	8 : 7.0
	1st wave	3.38	3.36	3.36	3.33	3.29	3.34
3,3'-	2nd wave	3.10	3.13	3.11	2.93	2.90	3.03
	ratio	8 : 7.3	8 : 7.4	8 : 7.4	8 : 7.0	8 : 7.0	8 : 7.3
	1st wave	3.54	3.35	3.34	3.33	3.32	3.38
4,4'-	2nd wave	3.18	3.23	3.23	3.12	3.09	3.17
	ratio	8 : 7.2	8 : 7.7	8 : 7.7	8 : 7.5	8 : 7.5	8 : 7.5
	1st wave	3.39	3.45	3.57	3.29	3.43	3.43
2,3'-	2nd wave	2.94	2.96	3.08	2.90	2.87	2.95
	ratio	8 : 6.9	8 : 6.9	8 : 6.9	8 : 7.1	8 : 6.9	8 : 6.9
	1st wave	3.50	3.55	3.51	3.64	3.60	3.56
2,4'-	2nd wave	3.26	3.09	3.98	3.23	3.07	3.13
	ratio	8 : 7.5	8 : 7.0	8 : 6.8	8 : 7.1	8 : 6.8	8 : 7.4
	1st wave	3.64	8.64	3.72	3.37	3.33	3.54
3,4'-	2nd wave	3.43	3.65	3.60	2.89	2.80	3.27
	ratio	8 : 7.5	3 : 8.0	8 : 7.8	8 : 6.9	8 : 6.7	8 : 7.4
	1st wave	3.50	3.48	3.51	3.41	3.37	
Mean	2nd wave	3.20	3.24	3.22	3.00	2.98	
	ratio	8 : 7.3	8 : 7.5	8 : 7.3	8 : 7.0	8 : 7.0	8 : 7.2

however, the reduction potential tends to shift to the negative side with the increasing pH. As a replacement of comparing the half-wave potential, comparison was made of the potential from the initial portion of the reduction potential to the point of inflexion to the latter stationary phase. As indicated in Fig. 3, the compounds possessing $-NO_2$ group in 2-position give reduction waves in narrower range of potentials than other isomers and the reduction potential shifts to the negative side in the order 2,3'-, 2,4'-, 3,3'-, 3,4'-, 4,4'-, 2,2'-, and diphenylarsinic acid.

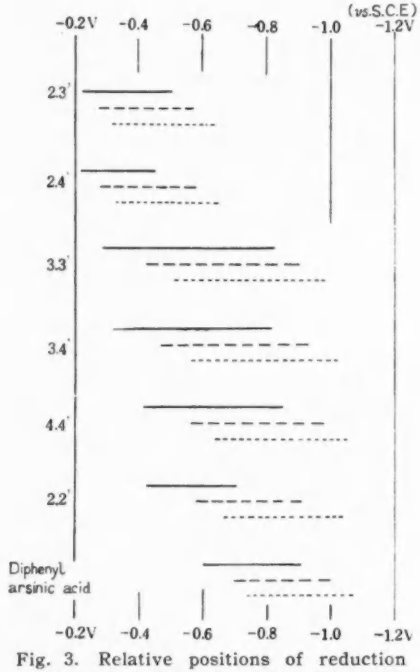
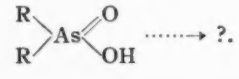


Fig. 3. Relative positions of reduction potential of the 2nd wave in Bis(nitrophenyl)arsinic acids
—— pH 1.04 - - - pH 2.2 ····· pH 3.0

Reduction mechanism of the 2nd wave will next be considered. As will be seen from Table III, the wave height of the 2nd wave is somewhat lower than that of the 1st wave on the acid side and the reduction that could be assumed for the 2nd wave will be in the reduction step of $-NO_2$ group,

$$-NHOH \xrightarrow[-H_2O]{2e+2H^+} -NH_2$$

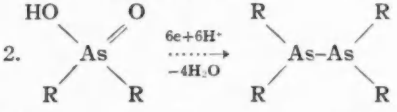
and



Considering the complicated wave form of the 2nd wave, these reactions must occur one after the other and the degree of duplication results in the variation of the breadth of the reduction wave potential, as shown in Fig. 3, and in the variation of wave form.

The number of electrons, n, taking part in the reduction was calculated according to the method of Gilbert and Rideal for the 2nd wave and the value of 7.3 for pH 2.2 was obtained in the 2,2'-compound. This result seems to indicate a seven-electron reduction but this is not necessarily conclusive. The value of n calculated for diphenylarsinic acid, without any $-NO_2$ group, was 3.2 and 3.3 at pH 2.2, indicating it to be a three-electron reduction. Since diphenylarsinic acid has the same structure as bis(nitrophenyl)-arsinic acids, with the exception of the absence of $-NO_2$ group, it was assumed that their diffusion coefficients would be approximately equal, and the polarogram of diphenylarsinic acid was taken under identical conditions as those for bis(nitrophenyl)arsinic acids. Subtraction of its wave height from that of the 2nd wave of bis(nitrophenyl)arsinic acids gave a value one-half of that of their 1st waves, i.e. corresponding to a 4-electron reduction from two $-NHOH$ to NH_2. Summarizing these facts, it may be assumed that the 2nd wave consists of four-electron reduction of two $-NHOH$ to $-NH_2$ and a three-electron reduction of arsenic. The following type may be considered for the reduction of arsenic:

2.



However, the state of reduction of diphenylarsinic acid may be vastly different and it would be too dangerous to conclude from these results that the foregoing facts indicate a three-electron reduction of arsenic. Further studies on this matter seem to be necessary.

(2) Effect of Various Factors on the Limiting Current of Bis(nitrophenyl)-arsinic Acids.

a) Relationship between Concentration and Limiting Current.—Polarograms of 2,2'-, 3,3'-, and 4,4'-compounds were taken in a buffer solution of pH 2.2 in various concentrations and the wave height of 1st and 2nd waves were measured. For example, the result of 2,2'-compounds is

presented in Table IV.

It is seen that there is a proportionality between the concentration and the limiting current in both the 1st and the 2nd wave in each of these compounds and i_d/C of the 1st and the 2nd wave in these compounds seem to be approximately equal.

TABLE IV
LIMITING CURRENT VS. CONCENTRATION

	2,2'-Bis(nitrophenyl)arsinic acid			
	1st wave		2nd wave	
Concentration (mM/l)	i_d (μamp.)	i_d/C (μamp./mM)	i_d (μamp.)	i_d/C (μamp./mM)
0.034	1.15	33.8	0.96	28.2
0.046	1.50	32.6	1.23	26.7
0.068	2.19	32.2	1.89	27.8
0.080	2.45	30.6	2.13	26.6
0.091	3.10	34.1	2.77	30.4
0.102	3.38	33.0	2.90	28.4
0.114	3.79	33.2	3.39	29.7
0.123	4.13	33.0	3.84	30.7
0.136	4.52	33.2	3.99	29.3
0.148	4.81	32.5	4.35	29.4
0.159	5.10	32.1	4.61	29.0
Mean		32.75±0.81		28.74±0.94

b) Relationship between Temperature and Limiting Current.—Limiting current of the 1st and the 2nd wave was determined from the polarograms of 2,2'-, 3,3'- and 4,4'-compounds in a buffer solution of pH 4.0, sample concentration being 2×10^{-4} M, at 30°, 25°, 20°, 15° and 10°C. The results obtained from the 1st wave indicate that there is a proportionality between the temperature and the limiting current in both 3,3'- and 4,4'-compound in this temperature range. The temperature coefficients of 3,3' and 4,4'-compounds in this case are 1.59 % and 1.61 %. These coefficients are appoximately equal to that in the case of ordinary diffusion current. The measurement was impossible with the 2,2'-compound since the solubilities decrease below 20°C, at this concentration and pH, and the compound precipitates out.

$$\left\{\left(\frac{i_d(t_1)}{i_d(t_2)}\right)^{1/t_2-t_1}-1\right\}\times100\%$$

c) Relationship between the Height of Mercury Reservoir and Limiting Current.—Polarograms of 2,2'-, 3,3'- and 4,4'-compounds in a buffer solution of pH 2.2, in a concentration of 1.14×10^{-4} M, with varying heights of the mercury reservoir and the wave heights of the 1st and the 2nd wave were measured. As indicated in Table V, the results of 2,2'-compound and diphenyl arsinic acid are presented only, a linear relationship was found to hold between the limiting current and the square root of the height of mercury reservoir $h^{1/2}_{eff.}$ In other words, these limiting currents do not contain any kinetic current but are controlled by the diffusion process.

(3) Determination of Bis(nitrophenyl)arsinic Acid Mixture.—As was

TABLE V
LIMITING CURRENT VS. EFFECTIVE HEIGHT OF THE MERCURY RESERVOIR 2,2'-BIS (NITRO PHENYL) ARSINIC ACID

$h_{eff.}^{1/2}$	1st wave		2nd wave	
(h:cm.)	i_d (μamp.)	$i_d/h_{eff.}^{1/2}$	i_d (μamp.)	$i_d/h_{eff.}^{1/2}$
9.19	5.66	0.63	4.98	0.54
8.63	5.29	0.61	4.61	0.53
8.03	4.99	0.62	4.41	0.55
7.38	4.58	0.62	4.04	0.55
6.67	4.18	0.63	3.57	0.54
5.87	3.71	0.63	3.20	0.55

Diphenyl arsinic acid
(concn.:2×10^{-4}M/l)

$h_{eff.}^{1/2}$ (h:cm.)	i_d (μamp.)	$i_d/h_{eff.}^{1/2}$
8.91	4.40	0.49
8.03	3.94	0.49
7.38	3.55	0.48
6.28	3.00	0.48

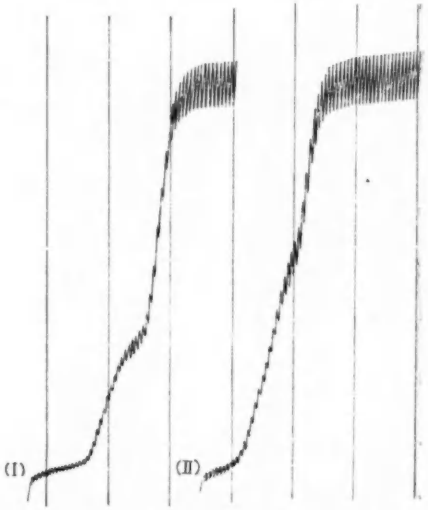


Fig. 4. Typical polarograms of synthetic mixtures of Bis(nitrophenyl)arsinic acids.
(I) 2,2'- : 3,3'- = 30 : 70(wt %)
(II) 2,2'- : 4,4'- = 50 : 50(,,)

mentioned earlier, the compounds possessing $-NO_2$ group in 2-position exhibit a reduction wave of the 1st wave in a more positive potential range than those with $-NO_2$ group in other positions and consequently show a divided wave (Fig. 4).

It follows, therefore, that the determination of a mixture of 2,2′- and 3,3′- or 4,4′-bis(nitropenyl)arsinic acid can be made concurrently by determining the 2,2′-compound from the 1st step in the 1st wave and 3,3′- or 4,4′-compound from the 2nd step wave that appears next. Tables VI and VII give results of determination carried out on several mixed samples by the standard addition method.

TABLE VI
DETERMINATION OF A SYNTHETIC MIXTURE OF 2,2′- AND 3,3′-BIS(NITROPHENYL)ARSINIC ACIDS

No.	Calculated Value (wt. %)		Observated Value (wt. %)	
	2,2′-	3,3′-	2,2′-	3,3′-
1	10.0	90.0	10.1	89.9
2	20.0	80.0	19.5	80.5
3	30.0	70.0	30.4	69.6
4	40.0	60.0	39.5	60.5
5	50.0	50.0	49.8	50.2
6	60.0	40.0	60.0	40.0
7	70.0	30.0	69.2	30.8
8	80.0	20.0	78.8	21.2
9	90.0	10.0	85.6	14.4

TABLE VII
DETERMINATION OF A SYNTHETIC MIXTURE OF 2,2′- AND 4,4′-BIS(NITROPHENYL)ARSINIC ACIDS

No.	Calculated Value (wt. %)		Observated Value (wt. %)	
	2,2′-	4,4′-	2,2′-	4,4′-
1	20.0	80.0	20.4	79.6
2	50.0	50.0	48.3	51.7
3	70.0	30.0	69.3	30.7

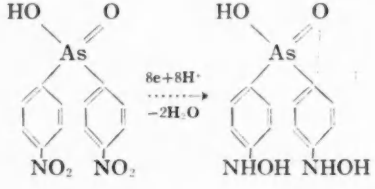
Separatory determination of a mixture of 3,3′- and 4,4′-bis(nitrophenyl)arsinic acids is impossible since such a mixture does not exhibit separate waves but the value of i_d/C is approximately equal in the two compounds so that the approximate value of the content can be obtained.

Mixtures of non-symmetrically substituted 2,3′-, 2,4′-, and 3,4′-compound cannot be determined although the presence of a compound with $-NO_2$ group in the 2-position can be detected from their 1st wave, as is evident from their reduction wave.

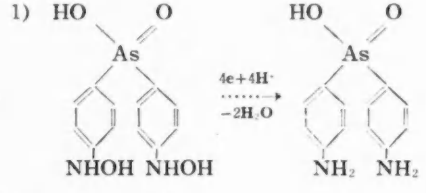
Summary

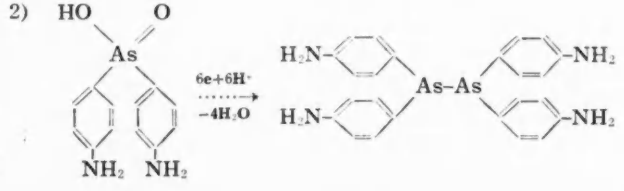
1) Polarographic behavior of the six isomers of bis(nitrophenyl)arsinic acid was considered and the waves can roughly be divided into 1st and 2nd waves in acid range at the dropping mercury electrode.

The 1st Wave:



The 2nd Wave:





2) The limiting current is controlled by the diffusion process and the Ilkovič equation is applicable.

3) The electrolytic reduction mechanisms of the 1st and 2nd waves are considered to be in the following manner, taking that of 4,4'-bis(nitropenyl)arsinic acid as an example: (see the figure of the preceding page).

4) By the utilization of the 1st wave, polarography can be used for the determination of bis(nitrophenyl)arsinic acids, especially those with the nitro group in 2-position.

The writers express their deep gratitude to Professor T. Sohmiya for much valuable advice during the course of this work and are grateful to Messrs. M. Ishiwatari and S. Yokouchi for supplying them with samples.

Engineering Research Institute
Faculty of Engineering
University of Tokyo
Hongo, Tokyo

*Polarography of Bis(aminophenyl)arsinic Acids, Phenylarsonic Acid and Arsanilic Acids**

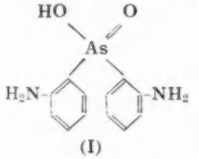
By Masao MARUYAMA and Toshiko FURUYA

(Received January 17, 1957)

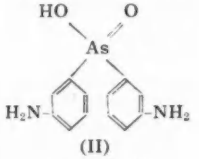
The writers stated in the preceding paper[1] that, on considering the polarographic behavior of bis(nitrophenyl)arsinic acids at the dropping mercury electrode, the 2nd wave that appears in an acid range may contain waves due to a three-electron reduction of arsenic. In order to further clarify this fact and also the polarographic behavior of organic arsenic compounds, reduction waves of bis(aminophenyl)arsinic acids, phenylarsonic acid, and arsanilic acids at the dropping mercury electrode were examined. The present paper also describes the results obtained from experiments on fundamental data for quantitative determinations.

Experimental

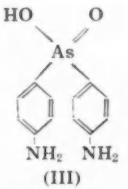
The four isomers of bis(aminophenyl)arsinic acids according to the position of the amino group, 2,2'-(I), 3,3'-(II), 4,4'-(III), and 3,4'-(IV), were used as the sample. Their respective melting points are shown with their structures:



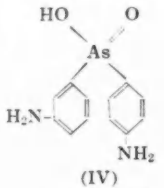
(I)
m.p. 154°C



(II)
m.p. 247°C

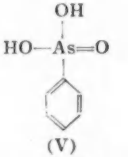


(III)
m.p. 223.5°C (decomp.)

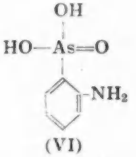


(IV)
m.p. 182°C

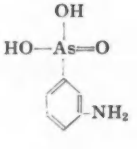
The melting points of phenylarsonic acid and arsanilic acids used for the experiment are as follows:



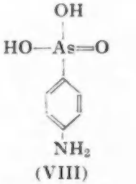
(V)
m.p. 158.5°C



(VI)
m.p. 144°C



(VII)
m.p. 207°C (decomp.)



(VIII)
m.p. 232°C

Experimental conditions and methods used in the present experiments were all the same as those described in the preceding paper[1].

* The gist of this work was presented at the symposium of the Japanese Society of Analytical Chemistry (May; 1955).

1) M. Maruyama and T. Furuya, This Bulletin., **30**, 647 (1957).

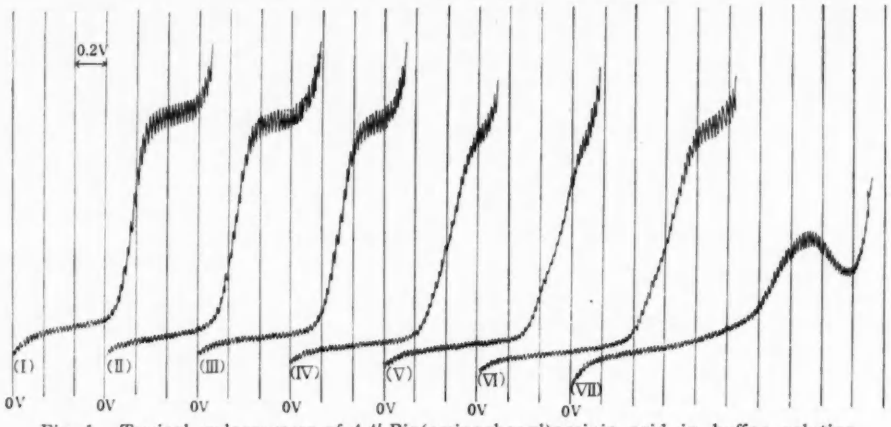


Fig. 1. Typical polarograms of 4,4'-Bis(aminophenyl)arsinic acid in buffer solution at various pH values.
(I) pH 1.04 (II) pH 2.2 (III) pH 3.0 (IV) pH 4.0 (V) pH 5.0
(VI) pH 6.0 (VII) pH 7.0

Experimental Results and Discussion

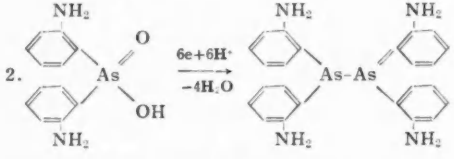
(1) **Reduction of Bis(aminophenyl) arsinic Acids in Buffers Solutions of Various pH.**—2,2'-, 3,3'-, 4,4'-, and 3,4'-Bis (aminophenyl)arsinic acids and diphenylarsinic acid show irreversible reduction wave below pH 7 (polarogram of 4,4'-compound at various pH is shown in Fig. 1 as an example). The wave form is a one-step wave at pH 1 to 3 and a complicated wave form, similar to that of diphenylarsinic acid, appears at pH 4 to 6. As was described in the preceding paper, diphenylarsinic acid shows a very similar, complicated wave form at pH 1 to 5 and an irreversible, three-electron reduction at around pH 2 to 3.

The half-wave potentials in all these compounds shift to the negative side with increasing values of pH, more markedly so in the 2,2-compound than the other isomers, and those of the other three isomers are very close together. The half-wave potentials of these compounds are indicated in Table I.

TABLE I
HALF WAVE POTENTIALS OF BIS(AMINOPHENYL)-ARSINIC ACIDS AT VARIOUS pH VALUES
$\pi_{1/2}$ mV(vs. S.C.E.).

pH	4,4'-	3,4'-	3,3'-	2,2'-
1.04	− 775	− 782	− 800	− 873
2.2	− 845	− 835	− 872	− 965
3.0	− 905	− 913	− 930	−1078
4.0	− 990	−1010	−1030	−1170
5.0	−1100	−1107	−1140	−1370
6.0	−1212	−1213	−1284	···

The wave height is approximately constant in the acid range, irrespective of pH, except for 2,2'-compound, and decreases suddenly at above pH 6. For the 2,2'-compound, the wave height tends to decrease somewhat with increasing pH values. As will be described later, the limiting current is controlled by the diffusion process and the number of electrons, n, taking part in the reduction, obtained by the microelectrolysis, was 3 for all the compounds at pH 2–3. These results suggest the following type as the reduction mechanism:



(2) **Effect of Various Factors on the Limiting Current of Bis(aminophenyl) arsinic Acids.**—

a) *Relationship between Concentration and Limiting Current:* The limiting current of 2,2'-, 3,3'- and 4,4'-bis(aminophenyl) arsinic acid and diphenylarsinic acid was measured in various concentrations in buffer solution of pH 2.2 and the results of 4,4'-compound and diphenylarsinic acid are presented in Table II. Other 2,2'-, 3,3'-compound had the same result.

b) *Relationship between Temperature and Limiting Current:* The results of measurement with various isomers and diphenyl arsinic acid indicate that the limiting

TABLE II

LIMITING CURRENT VS. CONCENTRATION

a) 4,4′-Bis(aminophenyl)arsinic acid

C(mM/l)	i_d(μamp.)	i_d/C(μamp./mM)
0.339	4.21	12.4
0.271	3.33	12.3
0.203	2.48	12.2
0.136	1.63	12.0
0.068	0.87	12.8
		12.35±0.41

As can be seen from Table II, a proportionality is established between the concentration and the limiting current in all these compounds.

b) Diphenyl arsinic acid

C(mM/l)	i_d(μamp.)	i_d/C(μamp./mM)
0.163	2.31	14.2
0.126	1.69	13.4
0.082	1.11	13.6
0.041	0.57	13.9
Mean		13.78±0.58

current increases in proportion to the rise of temperature and the temperature coefficients of 2, 2′-, 3, 3′-, and 4,4′-compound, dephenyl arsinic acid in this case are 1.36 %, 1.46 %, 1.39% and 1.38 %. These coefficients agree approximately with that in the case of diffusion current.

c) *The Relationship between the Height of Mercury Reservoir and Limiting Current:* The results of measurement with various isomers, (shown in Table III; the result of 4,4′-compound is shown as an example), indicate that a linear relationship exists between the limiting current and the square root of the height of the mercury reservoir, $h_{eff.}^{1/2}$, i. e. these limiting currents are controlled by the diffusion process.

TABLE III

LIMITING CURRENT VS. EFFECTIVE HEIGHT OF MERCURY RESERVOIR

4,4′-BIS(AMINOPHENYL)ARSINIC ACID

(Concn.: 3.39×10^{-4}M, pH: 2.2)

$h_{eff.}^{1/2}$(h: cm.)	7.75	8.06	8.37	8.66	8.94
i_d(μAmp.)	4.15	4.27	4.43	4.57	4.72
$i_d/h_{eff.}^{1/2}$	0.54	0.53	0.53	0.53	0.53

(3) **Reduction of Phenylarsonic Acid and Arsanilic Acids in Buffer Solutions of Various pH.**—The reduction wave of arsanilic acids appear at pH 1 to 3 and 2-, 3- and 4-arsanilic acid and phenylarsonic acid show irreversible waves with similar wave heights and wave forms (Fig. 2).

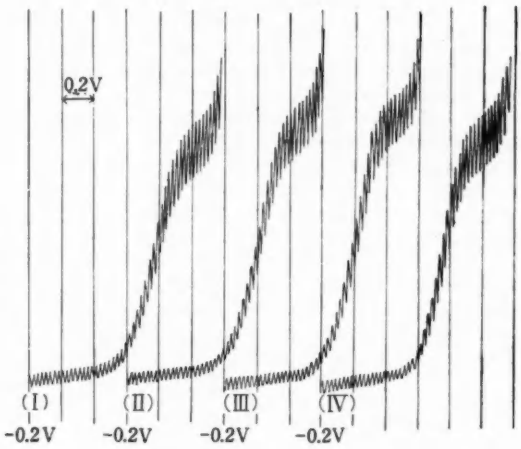


Fig. 2. Typical polarograms of arsanilic acids, phenylarsonic acid in buffer solution at pH 1.04.
(I) 2-Arsanilic acid
(II) 3-Arsanilic acid
(III) 4-Arsanilic acid
(IV) Phenylarsonic acid

The wave height is approximately constant at pH 1 to 3 but decreases rapidly at above pH 4. The half-wave potentials shift to the negative side with increasing pH values and the values tend to become negative in the order of phenylarsonic acid, and 2-, 3- and 4-arsanilic acid at the same pH, though the difference is very slight (Table IV).

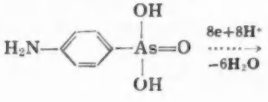
TABLE IV

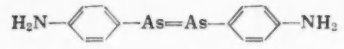
HALF-WAVE POTENTIALS OF PHENYLARSONIC ACID AND ARSANILIC ACIDS IN BUFFER SOLUTION

$\pi_{1/2}$mV. (vs. S.C.E.)

pH	Phenylarsonic acid	2-Arsanilic acid	3-Arsanilic acid	4-Arsanilic acid
1.04	− 955	− 960	− 976	− 985
2.2	−1060	−1072	−1080	−1098
3.0	−1175	−1176	−1175	−1185

The limiting current of these compounds is controlled by the diffusion process and the number of electrons, n, taking part in the reduction, obtained by the microelectrolysis, a buffer solution of pH 2.2, was approximately 4, indicating a four-electron reduction. If such is the case, the following type of reduction mechanism may be considered.





(4) Effect of Various Factors on the Limiting Current of Phenylarsonic Acid and Arsanilic Acids.—

a) *Relationship between Concentration and Limiting Current:* The results of measurement of limiting current of phenylarsonic acid and various isomers of arsanilic acid in a buffer solution of pH 2.2, at various concentrations, (as shown in Table V, the results of 4-arsanilic acid and phenyl arsinic acid are shown as an example), indicated that a linear relationship exists between concentration and limiting current.

TABLE V
LIMITING CURRENT VS. CONCENTRATION

a) 4-Arsanilic acid

C(mM)	i_d(μamp.)	i_d/C(μamp./mM)
0.538	10.67	19.8
0.428	8.42	19.7
0.321	6.27	19.5
0.214	4.17	19.5
0.107	2.08	19.4
Mean		19.59±0.20

b) Phenyl arsinic acid

C(mM)	i_d(μamp.)	i_d/C(μamp./mM)
0.520	10.30	19.8
0.416	8.42	20.2
0.312	6.17	19.8
0.208	4.07	19.6
0.104	1.94	18.7
Mean		19.61±0.77

b) *Relationship between Temperature and Limiting Current:* The results of measurement in a buffer solution of pH 2.2, indicated that the limiting current increases in proportion to the rise of temperature and the temperature coefficients of 4-, 3- and 2- arsanilic acid and phenyl arsinic acid are 1.27 %, 1.39 %, 1.28 % and 1.52 %. These coefficient agreed approximately with that in the case of diffusion current.

c) *Relationship between the Height of the Mercury Reservoir and Limiting Current:* The results obtained from the measurement in a buffer solution of pH 2.2, (shown in Table VI) (only 4-arsanilic acid and phenyl arsinic acid), indicate that a linear relationship is established between the square root of the height of the mercury reservoir, $h_{eff.}^{1/2}$ and the limiting current. Therefore, the limiting current does not contain a kinetic current but is controlled by the diffusion process.

TABLE VI
LIMITING CURRENT AND EFFECT HEIGHT OF MERCURY RESERVOIR

a) 4-Arsanilic acid (Conc.: 3.21×10^{-4}M)

$h_{eff.}^{1/2}$(h: cm.)	7.75	8.06	8.37	8.66	8.94
i_d(μamp.)	5.69	5.96	6.26	6.36	6.60
$i_d/h_{eff.}^{1/2}$	0.74	0.74	0.75	0.73	0.74

b) Phenyl arsonic acid (Concn.: 3.12×10^{-4}M)

$h_{eff.}^{1/2}$(h: cm.)	7.75	8.06	8.37	8.66	8.94
i_d(μamp.)	5.18	5.63	5.79	5.93	6.09
$i_d/h_{eff.}^{1/2}$	0.67	0.70	0.69	0.69	0.68

(5) Determination of Bis(aminophenyl)arsinic Acids in Arsanilic Acid.—The foregoing facts indicate that it is possible to determine bis(aminophenyl) arsinic acids and arsanilic acids individually by polarography but separatory determination of their isomers is impossible, considering the wave form and the half-wave potential of the reduction wave.

The problem in industrial process is the determination of bis(aminophenyl)arsinic acids in 4-arsanilic acid, the former being often present as an impurity in the latter during synthetic process. There has been no suitable method of determining this compound and some difficulties have been experienced.

However, the foregoing facts suggest the possibility of the utilization of polarographic method for this purpose. Actually, reduction at the dropping mercury electrode gives a separate wave (occurs first) by bis(aminophenyl)arsinic acids and its determination in 4-arsanilic acid is possible from this wave height.

Analytical results obtained with several kinds of synthetic sample are presented in Table VII.

TABLE VII
DETERMINATION OF BIS(AMINOPHENYL)ARSINIC ACID IN 4-ARSANILIC ACID

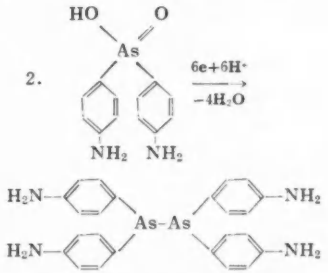
No.	Calculated Value (%) 4-Arsanilic acid	Calculated Value (%) Bis(aminophenyl) arsinic acid	Observated Value (%) Bis(aminophenyl) arsinic acid
1	85.0	15.0	14.0
2	70.0	30.0	30.1
3	60.0	40.0	41.7
4	40.0	60.0	56.0
5	20.0	80.0	76.0

Summary

1) Polarographic behaviors of bis (aminophenyl)arsinic acids, phenylarsonic

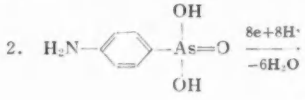
acid and arsanilic acids, were examined with dropping mercury electrode.

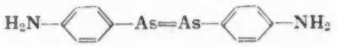
2) The reduction wave of bis(aminophenyl)arsinic acids appearing on the acid side is an irreversible three-electron reduction and this reduction mechanism is considered to be of the following type.



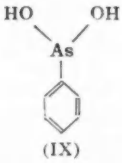
3) An assumption was forwarded in the preceding paper that the 2nd wave shown by bis(nitrophenyl)arsinic acids on the acid side may contain a reduction wave owing to the reduction of arsenic and that it is more likely to be a three-electron rather than a 4-electron reduction. The foregoing results obtained with bis(aminophenyl)arsinic acids suggest that it would be more appropriate to consider an irreversible, three-electron reduction.

4) The reduction waves shown by phenylarsonic acid and arsanilic acids on the acid side are an irreversible, four-electron reduction and the reduction mechanism may be assumed as follows:





5) Compounds like phenylarsinic acid (IX) do not exhibit a reduction wave at the dropping mercury electrode.



(IX)

6) Summarizing the foregoing facts, it may be concluded that these organic arsenic compounds which show a reduction wave at the dropping mercury electrode are quiquevalent arsenic compounds, the reduction wave is that of quinquevalent to tervalent, and that the compounds not possessing As=O are not reduced.

7) The limiting current of these compounds in the acid side is controlled by the diffusion process and is in proportional relationship with the concentration, so that it can be utilized for quantitative analysis.

The writers express their deep gratitude to Professor T. Sohmiya for much valuable advice during the course of this work and are grateful to Messrs. M. Ishiwatari and S. Yokouchi for supplying them with samples.

Engineering Research Institute
Faculty of Engineering
University of Tokyo
Hongo, Tokyo

Studies on the Mechanism of Eder's Reaction. I. Inducing Photochemical Reaction of Manganese(II)-Oxalate System

By Shukichi SAKURABA and Shozo IKEYA

(Received August 9, 1956)

Introduction

Since Eder's paper[1] (1880) the mechanism of the reduction of mercury(II) chloride to mercury(I) chloride with oxalate in a photochemically inducing system[2,3] or in the presence of an inducing catalyst[4,5] has long been studied. Considerable number of literature on the inducing action of $MnO_4^- - C_2O_4^{2-}$[6,7] or $Mn(III)-C_2O_4^{2-}$ system[8,9] are found but little has been done on $Mn(II)-C_2O_4^{2-}$ inducing system.

It has been previously reported that in a photochemical sensitive system of $Mn(II)-C_2O_4^{2-}$, mercury(II)chloride is quantitatively reduced to mercury(I) chloride[10]. The present investigation has been undertaken to elucidate the properties of an active intermediate formed by the ultraviolet irradiation on the solution containing the manganese(II) and the oxalate ion. They were persuaded by the estimation of its reducing power towards mercury (II) chloride and by the measurement of the change in absorbance of the reaction mixture.

This active intermediate appears to be correlated with the formation of active oxalic acid on the decomposition of manganese(III)-oxalate complex[11,12], and also with that of hydrogen peroxide on the oxidation of oxalic acid in the presence of the manganese(II) ion[13,14].

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12) F. R. Duke, ibid., **69**, 2885 (1947).
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Experimental Results

Material.—Sodium oxalate solution (0.100 M) was prepared from Merck's analytical grade chemical.

Manganese(II) sulfate solution (0.0140 M) was prepared from the guaranteed reagent labeled as containing below 0.002% Fe, and standardized by the Volhard method.

Mercury(II)chloride of extra pure grade was further recrystallized three times, and dissolved in water to produce 0.0489 M solution, its 1 ml. containing 0.01353 g. of mercury(II) chloride.

De-ionised water was used for all work.

Apparatus.—A low pressure mercury lamp (Kojima Type KY3C, 100V, 3A) was used for ultraviolet irradiation.

A model EPU quartz spectrophotometer (Hitachi, with 1 cm. cells) was used for all absorbance measurements.

Procedure.—To avoid an influence of the dissolved oxygen, nitrogen or carbon dioxide gas was passed through the test solution in a quartz flask for 40 min., then the solution was irradiated for various times. To examine the effect of dissolved oxygen, the solution was irradiated directly from the upside of the solution in the air. Experiments were carried out in the dark room.

1) Photochemical Reduction of Mercury (II) chloride to Mercury(I) chloride.

i) Formation of Mercury (I) chloride in the Absence of Oxygen.—To examine the effect of the manganese(II) ion on the photochemical reaction of mercury(II) chloride and oxalate, two kinds of solution were prepared as under annotation in Table I. A is 0.030 M sodium oxalate solution containing 0.1353 g. mercury(II) chloride per 50 ml. B is 0.030 M sodium oxalate solution containing 0.0001 to 0.002 M manganese(II)sulfate, and 0.1353 g. of mercury(II) chloride per 50 ml. In these solutions, no reaction occured in the dark at room temperature, regardless of the presence of the manganese(II) ion. When the solution was exposed to ultraviolet rays of mercury lamp after removal of dissolved oxygen, reaction took place instantly to form mercury(I) chloride. Experiments were done to analyse the effect of the concentration of the manganese(II) ion and of the hydrogen ion, on the reaction rate; the results are shown in Table I.

The presence of the manganese(II) ion makes the reduction rate about twice as great as in its absence (Table I, group 1). However, change in the manganese(II) ion concentration little affects the reduction rate in the range 0.0001 to

TABLE I
FORMATION OF MERCURY(I) CHLORIDE IN THE ABSENCE OF OXYGEN

Group of Expt.		No. of Expt.	$MnSO_4$ M./l.	pH	Hg_2Cl_2 found g.	%
Group 1.	A	1	0.	5.6	0.0450	38.3
	〃	2	0.	3.2	0.0441	37.5
	B	3	0.0001	5.6	0.0890	75.7
	〃	4	0.0001	3.2	0.0862	73.3
	〃	5	0.001	5.6	0.0813	69.1
	〃	6	0.002	〃	0.0862	73.3
Group 2.	B	1	0.002	5.6	0.1147	97.5
	〃	2	〃	4.0	0.1164	99.0
	〃	3	〃	3.2	0.1170	99.5
	〃	4	〃	1.8	0.1142	97.1

Total volume is 50 ml. Each solution is 0.030 M sodium oxalate, containing 0.1353 g. of mercury(II) chloride (corresponding to 0.1176 g. of mercury(I)chloride).; pH is controlled by sulfuric acid; A: Solution A. B: Solution B. Time of irradiation, 10 min. in Group 1; 30 min., in group 2.;

0.002 M; neither does the pH ragardless of the presence of the manganese(II) ion (Table I, group 1 and 2). Moreover in this reaction system, neither manganese(III) oxalate complex nor hydrogen peroxide is formed in the absence of oxygen. They are formed, however, in its presence in the same system.

ii) Formation of Mercury(I) chloride in the Presence of Oxygen.—The same solution in an equilibrium state with atomspheric oxygen was directly irradiated from upside, for an hour at 30°C. Results are given in Table II.

TABLE II
FORMATION OF MERCURY(I) CHLOLIDE IN THE AIR

Group of Expt.		No. of Expt.	$MnSO_4$ M./l.	pH	Hg_2Cl_2 found, g.	%
Group 3.	A	1	0.	3.2	a little	
	B	2	0.0001	〃	0.1169	99.4
	〃	3	0.001	〃	0.1168	99.3
	〃	4	0.002	〃	0.1175	99.9
Group 4.	B	1	0.002	5.6	0.0790	67.2
	〃	2	〃	4.0	0.1145	97.4
	〃	3	〃	3.2	0.1178	100.2
	〃	4	〃	1.8	0.0359	30.5

Total volume is 50 ml. Each solution is 0.030 M sodium oxalate, containing 0.1353 g of mercury(II) chloride (corresponding to 0.1176 g. of mercury (1) chloride); pH is controlled by sulfuric acid; Time of irradiation, 60 min. in Group 3 and 4.

It will be seen that in Solution A (without the manganese ion), the reaction is markedly inhibited by dissolved oxygen (Table II, group 3). However, in Solution B (containing the manganese ion) the reaction proceeds significantly, although inhibited by oxygen to some extent at a higher and a lower pH than about 3.2 (compare Table II, group 4 with Table I, group 2). Moreover, the upper part of Solution B assumed faint purpulish red, indicating the presence of manganese(III)-oxalate complex; the formation of hydrogen peroxide is also confirmed by the titanium method. These phenomena will be discussed below.

iii) Presence of an Active Intermediate.—In the experiments hither to described, the photochemical action was examined in solutions containing the manganese(II), the oxalate and the mercury(II) ion. The following experiments were carried out to ascertain that an active intermediate is produced in the solution containing neither mercury(II) chloride nor dissolved oxygen, and that it will remain active for a fairly long time and forms the manganese(III) ion and hydrogen peroxide in the atmosphere.

Two kinds of test solution were prepared: Solution C is 0.030 M sodium oxalate and Solution D is 0.030 M sodium oxalate solution, containing 0.002 M manganese sulfate. The pH of the solution was adjusted to 3.2 with surfuric acid. These solutions were irradiated for 30 min. under an atmosphere of carbon dioxide after removal of the dissolved oxygen. Being set aside for various times under an atmosphere of carbon dioxide after irradiation, each solution was treated with 10 ml. of the oxygen-freed mercury(II) chloride solution to make the total volume 50 ml. The resulting Solution C and D are named Mixture C and D, respectively.

The following phenomena were observed. In Mixture C no appreciable reduction took place immediately after irradiation, even if the mixture was exposed to the atmosphere. In Mixture D mercury(I) chloride was formed in the following manner: after 2 min., dense turbidity; after 30 min., apparent; after 3 hours, slight; after 20 hours, no turbidity. When these mixtures were exposed to the air, the precipitate was gradually increased in proportion to the initial quantity. Moreover, hydrogen peroxide was not produced in Mixture C and D in the atmosphere of carbon dioxide; it was formed, however, in Mixture D when this was exposed to the air. When Mixture D was exposed to the air and large quantity of mercury(I) chloride precipitated, the upper part of the solution assumed faint purplish red, indicating the presence of manganese(III) complex. When oxygen was vigorously passed through the irradiated Solution D for a few minutes, the solution losed its reducing power.

The experiments turned out as expected. An active intermediate is formed in the oxalate solution containing the manganese(II) ion by ultraviolet irradiation. The intermediate is able to reduce mercury(II) chloride even after interception of light and survives for several hours at room temperature in the absence of oxygen. When it reacts slowly with dissolved oxygen in the

presence of mercury(II) chloride, it forms a detectable amount of manganese(III) complex and hydrogen peroxide, but when it reacts with bubbling oxygen in the solution, it rapidly loses the activity.

2) Spectrophotometric Studies. — Further observation was spectrophotometrically made to ensure the presence of active intermediate. The active intermediate was first formed as an active state of manganese(II)-oxalate complex and at this stage no change in absorption appeared; its presence was indirectly ascertained by increase in the absorbance of manganese(III)-oxalate complex produced by the reaction of the active manganese(II)-oxalate and dissolved oxygen.

Composition of the solution in which the absorbance measurement was made is presented in Table III. Mixture 1 to 8 show the effect of the manganese(II) ion and pH on the absorbance; the absorption curve of some mixtures is shown in Fig. 1, indicating the presence of manganese (II)-oxalate complex and the active intermediate. Mixture 9 to 13 show the effect of varying manganese(II) ion concentration at a constant pH 3.2 (The absorption curve is not shown in Fig. 1).

TABLE III

COMPOSITION OF THE SOLUTION USED IN SPECTROPHOTOMETRIC OBSERVATION AND ABSORBANCE AT 260mμ

Mixture	$MnSO_4$ M./l.	pH	Absorbance at 260 mμ not irradiated	Absorbance at 260 mμ after irradiation
1	0	5.6*	0.087	0.087
2	〃	3.2	0.196	0.196
Ac	〃	2.3	0.203	0.203
3	0.005	5.6*	0.327	0.330
4	〃	4.8	0.310	0.391
5	〃	3.8	0.283	0.460
6	〃	3.2	0.265	0.515
7	〃	2.8	0.250	0.440
8	〃	1.4	0.237	0.375
9	0.001	3.2	0.216	0.435
10	0.003	〃	0.250	0.468
11	0.005	〃	0.265	0.515
12	0.007	〃	0.274	0.552
13	0.009	〃	0.282	0.539

All of the mixtures are 0.005 M/l. of $Na_2C_2O_4$, except Ac is 0.005 M./l. of oxalic acid only. pH is controlled by sulfuric acid.

* Sulfuric acid is not added.

i) Absorption Spectra of Manganese(II)-oxalate.——Data of the absorbance (Table III or Fig. 1) of these mixtures which were not irradiated, provide a qualitative information. When the oxalate solution is acidified with sulfuric acid or only contains oxalic acid, the absorbance increases with a little swelling at about 250 to 260 mμ as compared to the pure sodium oxalate solution. (Table III, 1 to Ac, or Fig. 1 curve 1, 2 and Ac). However, mixtures containing the

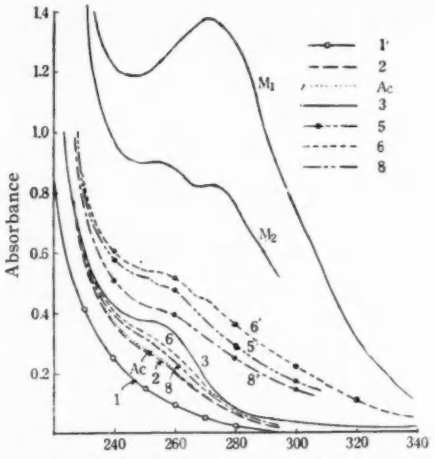


Fig. 1. Absorption curves of solutions containing oxalate and manganese(II) or mangnese(III) ion.
●: after irradiation (5', 6' and 8').

oxalate and the manganese(II) ion have a greater absorption swell at about 250 to 260 mμ than those without the manganese(II) ion (Fig. 1, curve 3, 6 and 8). Mixture 3 which does not contain sulfuric acid, has the largest absorbance over the range of about 250 to 260 mμ. When this solution is set aside overnight at room temperature, manganese(II)-oxalate crystallizes from the solution with a chemical composition of MnC_2O_4. The mixtures 4 to 8, the pH values of which were decreased with sulfuric acid, have lower absorbance than mixture 3 of a higher pH, although the absorbance of those mixtures is generally higher than that of free oxalic acid or a mixture of oxalate and sulfuric acid (compare curve 3, 6 and 8 with 1,2 and Ac in Fig. 1). Moreover, manganese(II)-oxalate did not crystallize from Mixture 4 to 8.

These observations suggest the presence of manganese(II)-oxalate complex which was pointed out by Malcolm and Noyes[15]. They showed that a solution containing manganese(II) perchlorate and sodium oxalate has an absorption at about 260 mμ and suggested that a manganese(II)-oxalate complex is formed in the solution, and this complex is regarded as the reactive species in the initial stage of the permanganete-oxalate reaction.

In Mixture 9 to 13 in Table III, the absorption curves are similar to the curve 6 in Fig. 1. The extent, to which the absorbance increases, becomes greater with increase in amount of the manganese(II) ion added, indicating a higher concentration of the manganes(II)-oxalate complex.

ii) Formation of Manganese(III). — Mixtures in Table III were irradiated for 30 min. at 20°C. in the atomosphere. In the absence

15) J. M. Malcolm and R. M. Noyes, *J. Am. Chem. Soc.*, **74**, 2769 (1952).

of the manganese(II) ion, the absorbance remained unchanged (Table III. 1, 2 and Ac), whilst in its presence it increases after irradiation (3 to 13 and curve 5', 6' and 8' in Fig. 1). This increase is due to the formation of manganese(III)-oxalate complex having an absorption maximum at 270 mμ*. To confirm this, further experiment was done as follows. When a few milligrams of solid manganese(III)-oxalate complex, $K_3[Mn(C_2O_4)_3]\cdot 3H_2O$**, were dissolved in the oxalate solution of a known pH, the absorption was observed as shown on curve M_1 in Fig. 1. The absorption curve gradually changed from M_1 to M_2 with time, owing to the decomposition of the manganese(III) complex to the manganese (II). It then approached to the curve 6 or 5 (which is omitted in Fig. 1) passing through the curve 6' or 5', according to the initial concentration of the complex salt and the pH of the solution. A quantitative treatment of the decomposition of manganese(III) complex will be discussed in the second report.

The formation of manganese(III) complex is most marked at pH 3.2 to 3.4 (Table III, No. 6 or Fig. 1. curve 6'). This is correlated to the fact that the reduction of Mercury(II) chloride most readily takes place at pH about 3.2 (Table II, pH 3.2 in Group 4). In the reaction mixture of pH 3.2, the quantity of the manganese(III) complex produced by irradiation, also increases with manganese(II) concentration to some extent (Table III. 9 to 13).

The formed manganese (III) complex decomposes gradually to manganese(II)-oxalate in the dark at room temperature, the absorption curve slowly recovering its original shape.

iii) Activation of Manganese-(II)-oxalate in the Solution. — The Mixture 6 in Table III was irradiated for 30 min. in the absence of oxygen. The formation of mercury(I) chloride was ascertained by the addition of mercury(II) chloride to a small portion of the mixture. The absorbance was measured with the remaining solution, the results being shown in Fig. 2. The absorbance remained unchanged for a long time in a current of carbon dioxide (Fig. 2. curve a-d). When the solution was exposed to air, however, the absorbance instantly increased (Fig. 2. curve c' and d') to an increasing extent with time (Fig. 2. c_1', c_2' and c_3'). However, it gradually decreased with further standing (Fig. 2. $c_3' \rightarrow c_4'$).

These phenomena can be accounted for as follow. The active intermediate formed by irradiation does not affect the absorbance of the solution in the absence of oxygen but changes it by the formation of

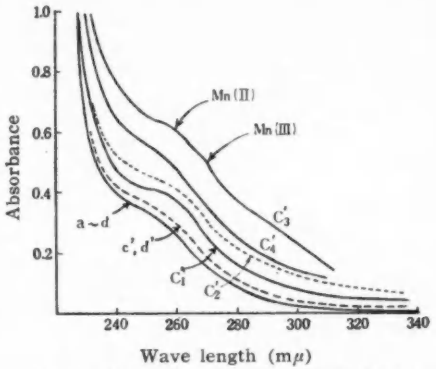


Fig. 2. Formation of manganese(III) by reaction between active intermediate and oxygen in the manganese(II)-oxalate system (at 8-10°C).
a: no treatment; b: irradiated for 30 min. in the absence of oxygen; c and d: b is set aside in the absence of oxygen for 30 min. and 51 hr., respectively; c': c is shaken in the air; d': d is shaken in the air; c_1', c_2', c_3' and c_4': c' is left exposed to air for 16, 20, 74 and 112 hr. respectivery.

manganese(III)-complex in the air even after interception of light. The decrease in absorbance with time is due to the reduction of manganese(III) to manganese(II). A slight swelling of the absorbance at about 270 mμ and 260 mμ in the curve of Fig. 2 may be caused by manganese (III) and manganese(II) oxalate complex, respectively (compare with curve M_1 and M_2 in Fig. 1).

The fact that, even after fifty hours the irradiated Mixture 6 kept in the atmosphere of carbon dioxide increased its absorbance when exposed to air, suggests that the active intermediate survives for a long time.

Discussion

Manganese(II)-oxalate is formed in the solution containing the manganese(II) and the oxalate ion, and an equilibrium is established as

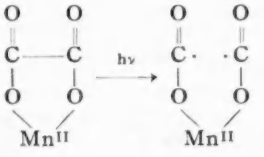
$$Mn^{2+} + C_2O_4^{2-} \rightleftharpoons MnC_2O_4 \quad (1)$$
$$MnC_2O_4 + 2H^+ \rightleftharpoons Mn^{2+} + H_2C_2O_4 \quad (2)$$

When the hydrogen ion concentration is low, manganese(II)-oxalate crystallizes (Table III, mixture 3). The absorption swell at about 250 to 260mμ is presumably due to the light absorption of manganese(II)-oxalate. The active state of manganese

* Part 2 of this series.
** This salt was prepared by the detail of Cartledge and Ericks[16].
16) G. H. Cartledge and W. P. Ericks, *J. Am. Chem. Soc.*, **58**, 2061 (1936).

(II)-oxalate by ultraviolet irradiation will result from the absorption of light quantum by manganese(II) oxalate molecules. This aspect is further supported by the fact that manganese(II)-oxalate is activiated even in the solid state by ultraviolet irradiation*. This fact also discloses that hydrogen ion does not take part in the activation of manganese(II)-oxalate molecule (step 2 and see Table III, 3 to 8).

Now, it seems that the C—C bond in the manganese(II)-oxalate molecule may be significantly loosened by steric strain. This effect should be controlled principally by the length of Mn—O bond. If this bond had ionic character, such an effect could be expected. Absorption of one light quantum of 300 mμ by a molecule is equivalent to the absorption of 100 Kcal. per mole, so that the energy of ultraviolet light is sufficient to rupture the bond. A conceivable mechanism could be as follows.



(3)

$$[I] + O_2 \longrightarrow [Mn^{II}—O—\dot{C}=O]^+ [II] + O_2^- + CO_2 \quad (4)$$

$$[Mn^{II}—O—\dot{C}=O]^+ + O_2 \longrightarrow Mn^{2+} + O_2^- + H_2O_2 \quad (5)$$

$$Mn(II) + O_2^- + 2H^+ \longrightarrow Mn^{3+} + H_2O_2 \quad (6)$$

$$[Mn^{II}—O—\dot{C}=O]^+ + Mn(III) \longrightarrow 2Mn^{2+} + CO_2 \quad (7)$$

$$[I] + Hg(II) \longrightarrow [II] + Hg(I) + CO_2 \quad (8)$$

$$[II] + Hg(II) \longrightarrow Mn^{2+} + Hg(I) + CO_2 \quad (9)$$

In this mechanism, step (3) is the activation of manganese(II)-oxalate molecule, resulting in the formation of a biradical [I]. When oxygen is present, the biradical [I] reacts rapidly to form the ion radical [II], O_2^- ion and carbon dioxide (step 4). The ion radical [II] further reacts with oxygen through step (5) to form manganese(II) ion, O_2^- ion and carbon dioxide. The O_2^- ion reacts rapidly with both manganese(II) and hydrogen ion, yielding manganese(III) and hydrogen peroxide (step 6)*. Hydrogen ion thus appears to be important in the formation of manganese(III) and hydrogen peroxide. Mixture 3 of pH 5.6 shows only negligible increase in absorbance after irradiation, indicating that the formation of manganese (III) complex is very slight in the deficiency of hydrogen ion. In mixture 8 of a high hydrogen ion concentration, the decrease in absorbance is again observed, presumably because of the decomposition of the manganese(III) complex. This fact is accounted for by step (5), (6) and (7)**. Therefore, optimum pH for the formation of manganese(III) complex is about 3.2.

It is well known that manganese(III) forms either red trisoxalato complex, $[Mn(C_2O_4)_3]^{3-}$, or yellow dioxalato complex, $[Mn(C_2O_4)_2(H_2O)_2]^-$, according to the oxalate ion concentration[17]. However, under the present experimental conditions, the complex in the solution was of so low a concentration, that the absorbance could be only measured in the ultraviolet region.

The photochemical catalytic action of the manganese(II) ion upon the formation of hydrogen peroxide in an oxalic solution is also accounted for by step (3) to (6).

The fact that the absorbance does not change in spite of the activation of manganese(II)-oxalate by irradiation (Fig. 2, b to d), may be possibly accounted for as follows. The concentration of activated manganese(II)-oxalate shoud be very low, and the absorbance swelling at about 250 to 260 mμ is possibly due to the absorption of Mn—O bond in manganese(II)-oxalate molecule and the fission of the C—C bond would not significently affect the absorption.

The reduction of mercury(II) chloride to mercury(I) occurs as steps (8) and (9), and in these steps the manganese(III) is not produced. A chain mechanism should be considered for the succeeding reaction system as in the case of the Hg(II)—Mn (III)—oxalate system[5].

Summary

Manganese(II)-oxalate is formed in the solution containing the manganese(II) and the oxalate ion and is activated by the ultraviolet absorption. The presence of this active manganese(II)-oxalate was

* This subject will be reported later.

* A kinetic treatment will be discussed in the later report.

** This will be discussed fully in second report of the series.

17) G. H. Cartlege and W. P. Ericks, *J. Am. Chem. Soc.*, **58**, 2065 (1936).

supported by the reducing power towards mercury(II) ions and by the spectrophotometric measurement. This active manganese(II)-oxalate reacts with oxygen and hydrogen ion to form hydrogen peroxide and manganese(III) oxalate complex.

The photochemical catalytic action of the manganese(II) ion upon formation of hydrogen peroxide in an oxalic acid solution appears to be due to the activation of manganese(II)-oxalate molecule.

Department of Chemistry, Faculty of Engineering Shizuoka University
Oiwake, Hamamatsu

Neue Synthetische Methode von Tetraphenyl-Phosphoniumhalogeniden

Von Yôichi HIRUSAWA, Mitsuo OKU und Kazumi YAMAMOTO

(Eingegangen am 21. Januar 1957)

Tetraphenyphosphoniumhalogenide finden jüngst auf dem Gebiete der analytischen Chemie als organisches Reagens Anwendung[1]. Im allgemeinen kann man das quartäre Phosphoniumhalogenid unmittelbar aus tertiärem Phosphin und Alkylhalogenid leicht darstellen:

$$R_3P + RX = R_4PX$$
(R=Alkylrest, X=Halogenatom)

Ist R aber dabei Phenyl, so findet diese Umsetzung überhaupt nicht statt. Mann[2] stellte Tetraphenylphosphoniumhalogenid aus Triphenylphosphin und Phenylhalogenid mit Hilfe von Aluminiumchlorid her.

Dodonow[3] und die anderen Forscher[4] erhielten es aus Phosphortrichlorid unter Anwendung von Grignard-Reagens.

Zwei von den Mitverfassern dieses Berichtes, Yamamoto und Oku, fanden eine rein katalytische, neue Methode zur Herstellung dieser Verbindung. Nach ihrer Methode kann man Tetraphenylphosphoniumhalogenide dadurch leicht herstellen, daß man Triphenylphosphin mit Phenylhalogenid in Methanol in Anwesenheit einer katalytischen Menge von Nickelhalogenid auf 150 bis 250°C erhitzt.

Die Umstzung verläuft leicht in der Reihenfolge von Chlorid, Bromid und Jodid und die Ausbeute beträgt an Chlorid 60%, und an Bromid und Jodid über 80%. Die Schmelzpunkte jeder Halogenide sind in der Tabelle I gegeben.

TABELLE I

Verbindung	Farbe	Schmelzpunkt °C
$(C_6H_5)_4PCl\cdot 5H_2O$	farblos	265
$(C_6H_5)_4PBr\cdot 2H_2O$	farblos	287
$(C_6H_5)_4PJ$	hellgelb	333

1. Analytische Methode der Tetraphenylphosphoniumhalogenide.

Die Verfasser bestimmten Phosphoniumhalogenid durch Argentometrie. Eine Probe wird mit 0,1 N $AgNO_3$ behandelt und dann mit 0,1 N KCNS unter Andwendung von Eisensulfat als Indikator zurücktitriert.

0,1 N $AgNO_3$ 1 ccm = 0,03745 g $(C_6H_5)_4PCl$,
0,0419 g $(C_6H_5)_4$ PBr, 0,0466 g $(C_6H_5)_4PJ$.

2. Beschreibung der Versuche.

In eine Ampulle von 80 ccm Inhalt werden die nötigen Mengen sowohl von Phenylhalogenid als auch von Triphenylphosphin, Methanol und Nickelhalogenid eingeschlossen und im Ölbad auf die bestimmte Temperatur erhitzt. Nach erfolgter Umsetzung bestimmt man den Phosphoniumgehalt im Reaktionsgemisch nach der Verdünnung mit Methanol (ca. 100 ccm). Alle Experimente wurden der Versuchsordnung gemäß durchgeführt. Zuerst wird über die Ermittelung der Bedingungen zur Darstellung von Tetraphenylphosphoniumbromid als Vertreter angegeben.

a) Einflüsse von Reaktionstemperatur, Reaktionsdauer, Luft und Verunreinigungen. — Die Experimente wurden unter folgenden Grundbedingungen gemäß dem Graeco-Latin Quadrat bestehend aus fünf Faktoren (Temperatur, Reaktionsdauer, Dibrombenzol und Wassergehalt von Brombenzol) in vier Gruppen durchgeführt.

1) H. H. Willard, *Ind. Eng. Chem., Anal. Ed.*, **11**, 186, 269, 305 (1939); W. T. Smith, *Anal. Chem.*, **20**, 937 (1948); H. A. Portratz, *Anal. Chem.*, **21**, 1276 (1919); **23**, 1680 (1951); M. Shinagawa, Vortrag bei der 8. Jahresversammlung der japanischen chemischen Gesellschaft (Nr. 14004) (1955).
2) F. G. Mann, *J. Chem. Soc.*, **1942**, 1192; **1942** 666, 1192.
3) J. Dodonow, *Ber.*, **61**, 907, (1928).
4) F. F. Bricke, *J. Am. Chem. Soc.*, **55**, 3056 (1933); **61**, 88 (1939); G. M. Kosolapoff, "Organophosphoros Compounds", John Wiley & Sons Inc. (1950), S. 78.
5) K. Yamamoto und M. Oku, J. P. 221,097 (zu Mitsui Chem. Ind. A. G.).

Grundbedingungen:

Triphenylphosphin	6,5 g	(1/40 Mol.)
Brombenzol	3,9 g	(1/40 Mol.)
Nickelbromid	0,11 g	(1/2000 Mol.)
Methanol	4,0 g	(1/8 Mol.)

Die Ordnungen und Resultate der Versuche sind in der Tabelle 2 zusammengefaßt.
Diese Resultate in die Tabelle der Streuungsanalyse zusammengefaßt erhält man die Tabelle III.

Aus diesen Resultaten ergibt sich:

1) Der Unterschied der Temperatur ist von grosser Bedeutung und die Temperatur von 160°C ist am besten.

2) Auch der Unterschied des Wassergehaltes von Brombenzol ist ebenfalls sehr wichtig und die Wasserfreiheit ist wünschenswert.

3) Der Unterschied von Dibrombenzolgehalt des Brombenzols ist etwas von Bedeutung.

4) Die Reaktion verläuft vorzüglicherweise unter der Atmosphäre von Stickstoff.

5) Die Wechselwirkung zwischen der Atmosphäre und dem Wassergehalt von Brombenzol ist sehr wichtig und zeigt, daß nachteilge Einflüße von Waser unter Atmosphäre von Stickstoff nur geringfügig sind.

6) Die Bedeutung zwischen den Reaktionsdauern in diesem Bereich kann man nicht beobachten.

b) ***Einflüsse von Reaktionsdauer, Molverhältnissen von Rohstoffen und geringen Mengen von Wasser in Brombenzol.***—Um die oben erhaltenen Resultate festzustellen, führten die Verfasser die Experimente gemäß dem anderen Latinquadrat bestehend aus vier Faktoren in drei Gruppen durch, wobei die Verfasser weitere Gebiete von Reaktionsdauern, geringere Wassergehalte und verschiedene Molverhältnisse von

TABELLE II

	Unter Luftatmosphäre				Unter N_2-Atmosphäre			
	T_4	T_2	T_1	T_3	T_4	T_2	T_1	T_3
W_4	A b	B d	C c	D a	A b	C c	B a	D d
	12,9	8,1	6,4	4,7	16,6	6,6	13,2	9.3
W_3	B c	A a	D b	C d	B d	D a	A c	C b
	25,0	10,0	4,2	9,5	37,6	27,7	12,4	16,6
W_2	C a	D c	A d	B b	C a	A d	D b	B c
	20,1	15,3	5,7	18,2	74,1	15,9	15,5	46,3
W_1	D d	C b	B a	A c	D c	B b	C d	A a
	47,4	29,3	38,6	35,7	64,6	24,5	39,4	32,8

W ist der Wassergehalt von Brombenzol (W_1=0%, W_2=3,3%, W_3=6,5%, W_4=12,1%), T die Temperatur (T_1=130°, T_2=140°, T_{33}=150° T_4=160°C), A, B, C und D sind die Reaktionsdauer (A=1, B=2, C=3, D=5 Std.) und a, b, c und d sind der Dibrombenzolgehalt (a=0%, b=7,2%, c=13,3%, d=23,5%). Die Ziffern in der Tabelle II zeigen die Ausbeute von Tetraphenylphosphoniumbromid (% d. Th. an Triphenylphosphin).

TABELLE III

	Faktoren	Summe der Abweichungsquadrate	Zahl der Freiheitsgrade	Quadrat der mitteleren Abweichungen	σ-Schätzung
T	Reaktionstemperatur	186222	3	62074	$9,55^{3+}$
W	Wassergehalt von Brombenzol	221250	3	23750	$11,34^{3+}$
	Reaktionsdauer	35619	3	11873	1,83
	Dibrombenzolgehalt	55320	3	18440	$2,84^{+}$
N	N_2-Atmosphäre	82070	1	82070	$12,62^{3+}$
	N×T	40645	3	13548	2,08
	N×W	245016	3	81672	$12,56^{3+}$
	Fehlerglieder	78036	12	6503	
	Insgesammt	944178	31		

wobei;	Überschreitungswahrscheinlichkeit	F^{1}_{12}	F^{3}_{12}
	1%	9,33	5,95
	5%	4,75	3,49
	10%		2,61

Brombenzol zu Triphenylphosphin gewählt hatten.

Die Grundbedingungen sind wie folgt:

Reaktionstemperatur	160°C
Methanol	0,1 Mol.
Triphenylphosphin	0,02 Mol.
Nickelbromid	1/3640 Mol.

Die Ordnungen und die Resultate der Experimente werden in der Tabelle IV zusammengefaßt.

TABELLE IV

Faktoren	Unter Luftatmosphäre			Unter N_2-Atmosphäre		
	t_1	t_2	t_3	t_1	t_2	t_3
W_1	M_1	M_2	M_3	M_1	M_2	M_3
	77,3	75,3	81,1	78,1	87,7	81,7
W_2	M_3	M_1	M_2	M_3	M_1	M_2
	72,2	77,3	77,4	79,9	83,5	82,3
W_3	M_2	M_3	M_1	M_2	M_3	M_1
	73,2	78,0	78,0	77,5	88,3	81,1

Wobei t die Reaktionsdauer ($t_1=3$, $t_2=5$, $t_3=7$ Std.), W der Wassergehalt von Brombenzol ($W_1=0$, $W_2=0{,}9$, $W_3=1{,}7\%$) und M das Molverhältnis von Brombenzol zu Triphenylphosphin ($M_1=0{,}9$, $M_2=1{,}0$, $M_3=1{,}1$) ist und die Ziffern in der Tabelle die Ausbeute von Tetraphenylphosphoniumbromid (% d. Th. an Triphenylphosphin) bedeuten. Die Tabelle V zeigt die Resultate der Streuungsanalyse.

Beobachtet man diese Resultate, so kann man folgende Verhältnisse verstehen:

1) Die Vorzüglichkeit der Reaktion unter Atomosphäre von Stickstoff wurde wieder festgestellt.

2) Der Unterschied zwischen diesen Reaktionsdauern ist von großer Bedeutung und die Reaktionsdauer von 7 Stunden ist am besten

3) Man kann die Wechselwirkung zwischen der Laufzeit in N_2-Atmosphäre im Bedeutungsniveau von 95% beobachten, d. h. unter N_2-Atmosphäre kann man die maximale Ausbeute bei der Reaktionsdauer von 5 Stunden erhalten, dagegen nimmt die Ausbeute unter der Luftatmosphäre mit der Reaktionsdauer geradlinig zu. (Es ist klar, wenn man das Verhältnis zwischen Ausbeute und Reaktionsdauer graphisch darstellt!)

4) Für das Molverhältniss von Dibrombenzol zu Triphenylphosphin und den derart kleinen Wassergehalt von Brombenzol kann man keine Bedeutung erkennen.

c) Darstellung der Tetraphenylphosphoniumhalogenide.—Aus den obigen Resultaten ergibt sich die folgende Normalarbeitsweise zur Darstellung von Tetraphenylphosphoniumbromid. Man setzt 26,2 g (0,1 Mol) Triphenylphosphin, 17,3 g (0,1 Mol) Brombenzol, 0,44 g (1/730 Mol) Nickelbromid mit 16 g (0,5 Mol) Methanol in einen Autoklaven (18 : 8 Stahl) von 130 ccm Inhalt ein. Nach dem Belüften mit Stickstoffstrom erhitzt man das Reaktionsgemisch fünf Stunden lang auf 160°C. Wenn man Methanol aus dem Reaktionsgemisch abdestilliert und dem zähen Rückstand ca. 200 ccm Wasser zusetzt, so scheiden sich feine Kristalle von Tetraphenylphosphoniumbromid aus. Nach der Umkristallisation kann man 36,4 g von reinem Bromid erhalten (80% d. Th.).

Auch Tetraphenylphosphoniumjodid kann man auf gleiche Weise unter Anwendung von Jodobenzol anstatt des Brombenzols in einer Ausbeute von über 90% erhalten. Dagegen ist die Synthese des entsprechenden Chlorids ziemlich schwer und bedarf noch höherer Reaktionstemperaturen. Die Ausbeute beträgt 23% bei 180° und 60% bei 230°C. Also ist es zweckmäßiger, nach der Methode von Blicke[6] Chlorid mittelbar aus Bromid herzustellen.

3. Betrachtung über den Reaktionsmechanismus. — Die Mitverfasser dieses Berichtes, Yamamoto und Oku[7] teilten früther mit, daß Bistriphenylphosphin-Nickelbromid-Bisphenylbromid, $[(C_6H_5)_3P]_2NiBr_2 \cdot 2C_6H_5Br$, das als Katalysator für die Herstellung von Acrylester nach dem Reppe-Verfahren verwendet wird, durch Methanol zu Nickelbromid

TABELLE V

	Faktoren	Summe der Abweichungsquadrate	Zahl der Freiheitsgrade	Quadrat der mitteleren Abweichungen	σ-Schätzung
t	Reaktionsdauer	9097	2	4549	$11,3^{3+}$
W	Wassergehalt	623	2	312	0,77
M	Molverhältnis	551	2	273	0,68
N	N_2-Atmosphäre	14056	1	14056	$34,9^{3+}$
	$t \times W$	3827	2	1914	4.75^{2+}
	Fehlerglieder	3220	8	403	
	Insgesammt	31274	17		
Wobei:		Überschreitungswahrscheinlichkeit	F_s^1	F_s^2	
		1%	11,26	8,65	
		5%	5,32	4,46	

6) F. F. Blicke. *J. Am. Chem. Soc.*, **70**, 737 (1948).

7) K. Yamamoto und M. Oku, dieses Bulletin, **27**, 511 (1954).

und Tetraphenylphosphoniumbromid zersetzt wird.

Betrachtet man nun den Reaktionmechanismus auf Grund dieser Tatsache, so kann man leicht vermuten, daß diese Reaktion die Zwischenkatalyse von Nickelbromid (unter Bildung der oben genannten Komplexverbindung) verläuft. In der Tat beobachtet man, daß das Reaktionsgemisch während der Destillation des Methanols die charakteristische grüne Farbe von $[(C_6H_5)_3P]_2NiBr_2 \cdot 2C_6H_5Br$ aufweist. Folglich kann der Mechanismus dieser Reaktion mit folgenden Gleichungen gezeigt werden:

$$2(C_6H_5)_3P + NiBr_2 + 2C_6H_5Br = [(C_6H_5)_3P]_2NiBr_2 \cdot 2C_6H_5Br$$

$$[(C_6H_5)_3P]_2NiBr_2 \cdot 2C_6H_5Br = 2(C_6H_5)_4PBr + NiBr_2$$

$$2(C_6H_5)_3P + 2C_6H_5Br = 2(C_6H_5)_4PBr$$

Diese Reaktion geht überhaupt nicht in solchem Lösungsmittel vor sich, wie Aceton oder Cyclohexanon, das die Komplexverbindung stabil auflösen kann. So kann Methanol nicht nur für Lösungsmittel, sondern auch für Katalysator gelten.

TABELLE VI

	°C	%(Gew.)	°C	%(Gew.)
$(C_6H_5)_4PJ$	20,8	0,15	80,0	0,72
	40,2	0,18	99,8	1,55
	58,5	0,36		
$(C_6H_5)_4PBr$	20,8	1,72	59,8	7,68
	40,0	3,13	79,3	13,07
$(C_6H_5)_4PCl$	20,5	16,29		
	80,0	62,80		

4. Löslichkeit von Tetraphenylphosphoniumhalogeniden.—Die Resultate von den Bestimmungen der Löslichkeiten der Tetraphenylphosphoniumhalogenide in Wasser sind in der Tabelle VI zusammengefaßt.

Zusammenfaßung

Die Verfasser fanden eine katalytische Methode zur Herstellung von Tetraphenylphosphoniumhalogeniden heraus. Und die optimalen Reaktionsbedingungen wurden den Versuchsordnungen gemäß festgestellt. Nach dieser Methode kann man Tetraphenylphosphoniumhalogenide dadurch in hoher Ausbeute leicht herstellen, daß man Triphenylphosphin mit Phenylhalogenid in Methanol in Anwesenheit einer katalytischen Menge von Nickelhalogenid 5 bis 7 Stunden lang auf 160° bis 250°C erhitzt. Die Verfasser nehmen an, daß diese Reaktion durch die Zwischenkatalyse von Nickelhalogenid vor sich geht.

Zum Schluß bezeigen die Verfasser ihre Dankbarkeit dem Herrn Dr. K. Yoshikawa für seine eifrige Leitung und der Mitsui Chemischen Industrie A. G., die ihnen die Veröffentlichung dieser Arbeit erlaubte.

(Vorgetragen am 25. 11. 1956 bei der Versammlung der Kyushu-Zweigabteilung der japanischen chemischen Gesellschaft)

Mitsui Chemische Industrie A. G.
Miike Farbestoffwerk
Omuta, Fukuoka

SHORT COMMUNICATIONS

Studies on Amino-hexoses. V. An Improved Preparation of D-Arabinose via Oxidation of D-Glucosamine

By Yoshio MATSUSHIMA and Masayo OGAWA

(Received February 25, 1957)

The Ruff degradation of calcium D-gluconate, a practicable method of preparing D-arabinose, was much improved and 41 to 46% theoretical yield was secured in obtaining a practically pure specimen[1]. One of the present authors reported previously that the hypochlorite oxidation of D-glucosamine resulted in the formation of D-arabinose, ammonia and formic acid and the conditions suitable for preparing crystalline specimen were recorded[2]. The main cause of the difficulty was contamination of a large amount of inorganic salts in the reaction mixture. The introduction of ion-exchangers now available has enabled the authors to overcome the difficulty and a good yield of practically pure D-arabinose has been obtained. The ion-exchangers remove inorganic salts, residual glucosamine and colored impurities, and the concentration of the aqueous solution affords immediately raw crystals. Paper chromatography reveals no formation of sugars other than D-arabinose.

Experimental

A mixture of 21.6 g. of D-glucosamine hydrochloride, 100 ml. of water and some 200 g. of cracked ice is placed in a beaker surrounded by ice and salt. Under mechanical stirring a solution of 4 g. of sodium hydroxide in 20 ml. of water is added and sodium hypochlorite solution equivalent to 7.1 g. of chlorine is dropped in. After consumption of the oxidant the reaction mixture is neutralized to pH 3 with 6 N hydrochloric acid and is concentrated in vacuo as far as possible. The resulting mixture of salts and colored syrup is mixed with 50 ml. of ethanol, filtered and washed thoroughly with 70% ethanol. The ethanolic solution is diluted with water to about 300 ml. and passed alternately through the columns of Amberlite IR-120 and Dowex-2. The combined solution and washings give, after concentration in vacuo, crystals melting at 153° (uncorr.) when once recrystallized from aqueous methanol. $[\alpha]_D$ (final) −104.6° (c, 3.26; water). The yield reaches 45 to 48% of theory.

Department of Science, Nara Women's University, Nara

1) H. G. Fletcher, Jr., H. W. Diehl and C. S. Hudson, *J. Am. Chem. Soc.*, **72**, 4546 (1950).
2) Y. Matsushima, This Bulletin, **24**, 17 (1951).

Syntheses of New Phenylfluorone Derivatives and their Reaction with Metal Ions

By Hirotoshi SANO

(Received April 23, 1957)

Although numerous investigations have been published on the colorimetric determinations of germanium, tin, titanium and zirconium with phenylfluorone (abbr. of 2,3,7-trihydroxy-9-phenylfluorone), researches for phenylfluorone derivatives are insufficient. Only 2,3,7-trihydroxy-9-(4′-dimethylaminophenyl)-fluorone has been synthesized by the author and his coworkers[1]. Subsequently, some derivatives were synthesized by a similar procedure. 2,3,7-Trihydroxy-9-(3′-nitrophenyl)-flurone, 2,3,7-trihydroxy-9-(4′-nitrophenyl)-fluorone and 2,3,7-trihydroxy-9-(2′-sulfophenyl)-fluorone were obtained. These compounds have never been described in the literature of the subject except the 3′-nitro derivative[2].

Procedure for Synthesis.—Twenty g. of the benzaldehyde derivative concerned was dissolved in 300 ml. of 20% ethanol. To the solution were added 100 ml. of ethanolic solutions, containing 70 g. of hydroxyhydroquinone triacetate and 10 ml. of concentrated sulfuric acid or 30 ml. of concentrated hydrochloric acid. The solution was heated on a steam bath for about three hours, and allowed to stand for a week. The yellow or red crystalline precipitate was filtered and suspended in water at pH 4. The hydrolyzed precipitate was filtered, washed and dried in a vacuum desiccator. The yields of 3′-nitro, 4′-nitro, and 2′-sulfo derivative are 21, 30, and 28%

1) K. Kimura, H. Sano and M. Asada, This Bulletin, **29**, 640(1956).
2) E. Heintschel, *Ber.*, **38**, 2878 (1905).

of the theoretical, respectively.

Anal. of the 4'-nitro derivative. Found: C, 60.25; H, 3.27. Calcd. for $C_{19}H_{11}O_7N$: C, 62.47; H, 3.04%.

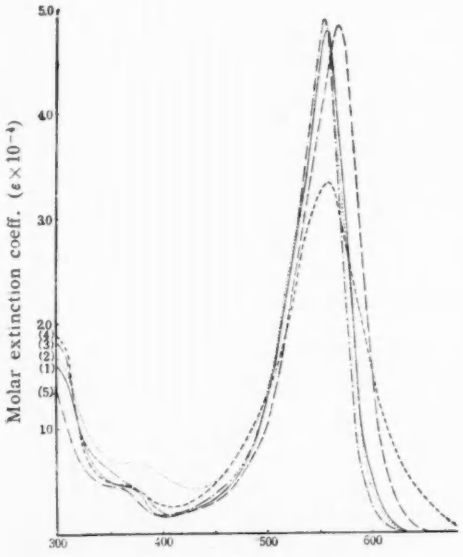


Fig. 1. Absorption spectra of products in alkaline media.

Curve (1) —— Phenylfluorone.
Curve (2) ····· 4'Dimethylaminophenylfluorone.
Curve (3) — — 3'-Nitrophenylfluorone.
Curve (4) ------ 4'-Nitrophenylfluorone.
Curve (5) —·— 2'-Sulfophenylfluorone.

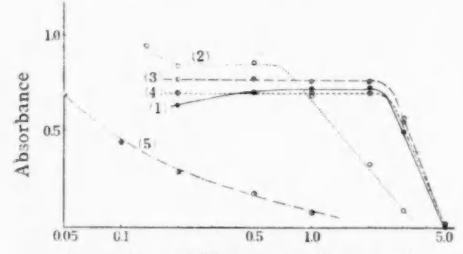


Fig. 2. Effect of acidity on germanium-fluoronates with germanium concentration fixed.

Curve (1) Phenylfluorone (510 mμ).
Curve (2) 4'-Dimethylaminophenylfluorone (510 mμ).
Curve (3) 3'-Nitrophenylfluorone (520 mμ).
Curve (4) 4'-Nitrophenylfluorone (520 mμ).
Curve (5) 2'-Sulfophenylfluorone (500 mμ).

Anal. of the 2-sulfo derivative. Found: C, 56.03; H, 3.35. Calcd. for $C_{19}H_{12}O_8S$: C, 57.01; H, 3.02%.

Properties of the Products.—The products do not melt below 270°C. The colors of 3'-nitro, 4'-nitro and 2'-sulfo derivative, are red, brownish red, and orange respectively. 3'-Nitro and 4'-nitro derivative are difficultly soluble in water but slightly soluble in ethanol. 2'-Sulfo derivative is slightly soluble both in water and in ethanol. Addition of acid or base to the ethanolic solution increases the solubility. The absorption spectra in strongly alkaline solutions are analogous to that of phenylfluorone or 4'-dimethylaminophenylfluorone as shown in Fig. 1. The absorption maxima shift toward longer wavelength in the cases of 4'- and 3'-nitro derivative, as is expected from the *I*- or *E*- effect of the nitro group. On the other hand the absorption maximum shifts toward shorter side in the case of 2'-sulfo derivative, suggesting that the effect of the phenyl group is reduced by the steric hindrance of the sulfo group. These facts convince the author that the products correspond to the compounds named.

Reactions with Metal Ions.—These compounds react with metal ions such as germanium, tin, titanium and zirconium, in adequate conditions. For instance the reactivities of the compounds with germanium at various acidities are illustrated in Fig. 2, including those of the phenylfluorone and the 4'-dimethylaminophenylfluorone for the comparison. The reactivity increases with increasing *I*- or *E*-effect of the substituent. The germanium complexes of 4'- or 3'-nitrophenylfluorone are slightly soluble in ethanolic solution, whereas that of 2'-sulfophenylfluorone is soluble to the same extent as the 4'-dimethylaminophenylfluorone chelate. These suggest that the compounds are useful for the colorimetric determinations of germanium. The complexes with other metals show a similar tendency in the reactions. The other derivatives such as 3',5'-dinitro, 3'-amino, or 4'-sulfophenylfluorone are under investigation. Detailed information on the compounds and their metal chelates will be published before long.

The author is indebted to Mr. Shozo Masuda of this University for the organic analyses of the products.

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo

Crystallization of Amorphous Nickel Sulfate

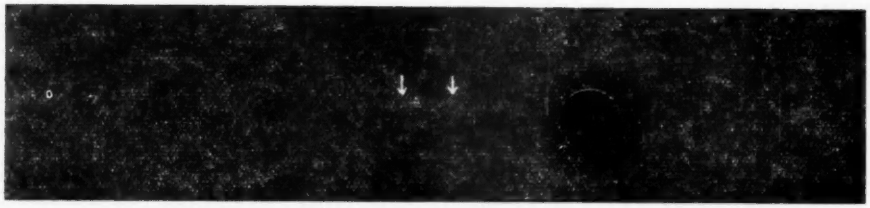
By Hideaki CHIHARA and Syûzô SEKI

(Received May 30, 1957)

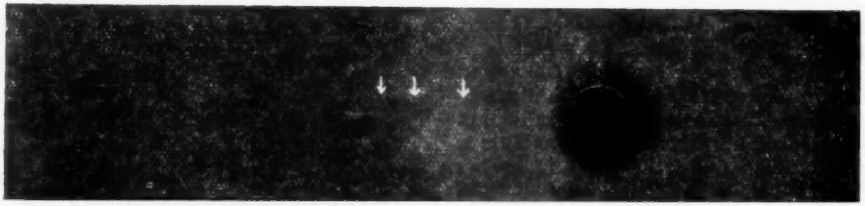
While working with the dehydration of a series of hydrates of nickel sulfate[1], crystallization of amorphous nickel sulfate was observed. Kahlbaum nickel sulfate was used to obtain the hexahydrate from aqueous solution. The hexahydrate structure[2] being identified by the X-ray powder method, the crystals were dehydrated on a quartz helical balance under vacuum less than 10^{-5} mm Hg, at temperatures up to 250°C until a constant weight was reached (four hours at 130° and an hour at 250°). The initial formula was calculated to be $NiSO_4 \cdot 5.98H_2O$ on the basis of complete dehydration.

The anhydrous nickel sulfate was brown in color and soluble in water (thus not nickel oxide). The X-ray pattern taken in a closed glass capillary with Cu K_α radiation showed that it was amorphous with two hardly discernible haloes (Fig. 1). Annealing at 100°C made the haloes progressively sharper and an additional halo appeared at a larger diffraction angle. Fig. 2 is the result obtained after four hours annealing at 100°C. Further heating at 110°C for six hours brought about sharp Debye rings as shown in Fig. 3, which remained unchanged on further heating. The observed spacings together with the relative intensities obtained by a recording microphotometer are listed in the accompanying table.

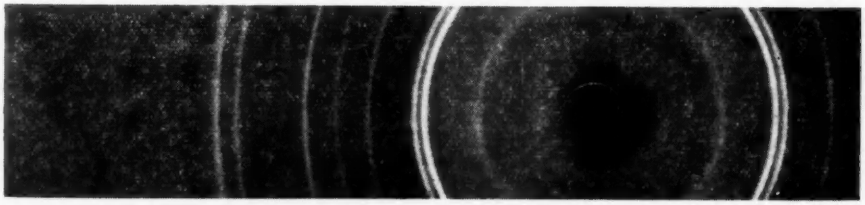
A survey of the literature revealed that F. Hammel reported[3] that the anhydrous nickel sulfate is orthorhombic with the unit cell of dimensions $a=4.6_2$, $b=6.5_1$, and $c=8.4_9$A. The present result is, however, consistent neither with this unit cell nor with the pattern given by Hammel. A



1. Anhydrous $NiSO_4$, amorphous.



2. Anhydrous $NiSO_4$, annealed at 100°C., 4 hours, amorphous.



3. Anhydrous $NiSO_4$ annealed further at 110°C., 6 hours, crystalline.

1) H. Chihara and S. Seki, This Bulletin, **26**, 88 (1953).
2) C. A. Beevers and H. Lipson, *Z. Krist.*, **83**, 123 (1932).
3) F. Hammel, *Compt. rend.*, **202**, 57 (1936).

TABLE

Spacing in Å.	Intensity	Tentative index based on the tetragonal cell
4.72	15	200
3.32	130	111
3.16	95	300
2.55	40	211
2.25	35	301
2.19	5	311
2.16	5	—
2.02	75	321
1.88	20	411
1.80	15	—
1.78	20	421
1.76	10	520
1.74	5	
1.66	50	440
1.63	10	550, 002, 551
1.58	70	600, 112
1.57 (shoulder)	35	
1.45	15	222, 531
1.44	10	302, 601
1.27	18	422

comparison of ionic radii of bivalent cations (Mg^{++} 0.65Å, Ni^{++} 0.70Å, and Zn^{++} 0.74Å) suggests that nickel sulfate may well be isomorphous with $MgSO_4$ and/or $ZnSO_4$. The anhydrous nickel sulfate prepared in a different manner from Hammel's may crystallize in a different way. A possibility will be open for finding other modifications of sulfate of metals of the magnesium series.

An attempt was made to assign a unit cell to the new modification which can reasonably account for the observed spacings. There are not fewer than three possibilities. The simplest one is indicated in the third column of the table. This is of simple tetragonal cell with dimensions $a=9.5_4$Å and $c=3.2_5$Å (the volume of the unit cell is 300Å^3). An orthorhombic unit cell with dimensions $a=6.9_2$Å, $b=6.3_1$Å, and $c=4.7_1$Å or with dimensions $a=10._0$Å, $b=7.9_3$Å, and $c=4.7_7$Å can equally well or better reproduce the observed spacings, the volume of the unit cell being 200 and 380Å^3, respectively. These orthombic cells are considered to be less probable in view of the too small or too great unit cell volume. A trial of finding the crystal class and the unit cell in an unarbitrary way was also made by Ito and Sadanaga's method[4], unsuccessfully, owing to lack of accuracy in the determination of the diffraction angle.

Department of Chemistry, Faculty of Science, Osaka University, Nakanoshima, Kita-ku, Osaka

4) T. Ito, X-ray Studies on Polymorphism, Maruzen Co. Ltd., Tokyo, (1950).

Separation of a Trace Amount of Cesium from Large Amounts of Potassium or Ammonium by Coprecipitation with Thallium (I) Chloroplatinate

By Noboru YAMAGATA and Eisaku TAJIMA

(Received April 26, 1957)

The carrier-free separation of cesium by the thallium (I) dipicrylaminate method from fission products is successful only when both potassium and ammonium ions are absent[1]. However, it is sometimes

TABLE I

SOLUBILITY OF ALKALI CHLOROPLATINATES IN WATER

(g. anhydrous salt per 100 g. water at 20°C)

K	0.7742
NH_4	0.5000
Rb	0.0283
Cs	0.0086
Tl (I)	0.0064 (15°C)

TABLE II

SEPARATION OF CESIUM-137 FROM POTASSIUM AND AMMONIUM

(at room temperature)

Solution (30ml.)	Thallium (I) added mg.	Chloroplatinic** acid added ml.	Cesium-137 coprecipitated
0.3 N KCl	20	1	54.0
0.1 N KCl	20	1	79.1
0.1 N KCl	20	1.5	81.4
0.1 N KCl	40	2	81.0
0.03 N KCl	40	2	83.1
0.1 N KCl*	20	1.5	77.1
0.3 N KNO_3	20	1.5	57.9
0.3 N KNO_3	40	1	47.0
0.1 N KNO_3	20	1.5	82.0
0.1 N KNO_3	20	1.5	82.0
0.1 N KNO_3	10	0.75	51.3
0.1 N KNO_3	5	0.38	19.0
0.3 N NH_4Cl	20	1	71.0
0.1 N NH_4Cl	20	1	78.9

* 5 μg. of cesium added.
** 5% aqueous solution.

1) This Bulletin, **30**, 580 (1957).

required to separate a trace amount of cesium from a large amount of these ions, especially from potassium.

The solubility of chloroplatinates of alkali metals and thallium (I) in water, as shown in Table I[2], indicates the possibility of the coprecipitation of a small amount of cesium with thallium (I) chloroplatinate in the presence of a large amount of potassium or ammonium ions.

A tracer experiment by the use of cesium-137 was performed to confirm this presumption; the procedure is the same as described in the previous report[3]. The results are shown in Table II; carrier-free cesium-137 or a microgram quantity of cesium can be separated from about 0.1 g. potassium in chloride or nitrate solution with a yield of about 80%. As the solubility of thallium (I) chloride is comparatively greater (0.29 g./100 g. water at 15.6°C)[4] than that of thallium (I) chloroplatinate, the formation of the precipitate of the latter is not interfered with by the presence of a large amount of chloride ions.

The precipitated thallium (I) chloroplatinate is dissolved in hot hydrochloric acid containing chlorine. The resulting solution, after being boiled to expel excess of chlorine, is made 2 N hydrochloric acid and passed through an anion-exchanger column (Dowex 1, X-8, ϕ 5×50 mm.). The effluent, free from thallium (III) and platinum (IV), contains 100% of the coprecipitated cesium and only a trace of potassium.

Kiriu College of Technology
Gumma University, Kiriu

2) A. Seidell, "Solubility of inorganic and metal organic compounds", New York, (1940) p. 456, 1086, 1424, 1434.
3) This Bulletin, **30**, 577 (1957).
4) "Gmelin's Handbuch der anorganischen Chemie" Thallium, p. 273.

Photometric Determinations of Indicator End Points in Complexometric Titrations

By Sôichirô Musha, Makoto Munemori and Kin'ya Ogawa

(Received July 4, 1957)

In photometric titrations with indicator, the color does not develop linearly with increasing amount of the added titrant. This characteristic has been elucidated by the mathematical treatment of complexometric titrations with a metal indicator[1]. A similar objection which is presented in the neutralization titration could be overcome by Higuchi, Rehm and Barnstein[2], but their method can not be applied directly to the complexometric titration.

In the titration of a metal with such a reagent as Complexon-III (disodium ethylenediamine tetra-acetate) in an aqueous system, there is the following equilibrium:

$$MI+Y^*=MY+I^* \qquad (1)^{**}$$

The equilibrium constant, K, is given by

$$K=[MY][I^*]/[MI][Y^*]=K^*_Y/K_I^* \qquad (2)$$

where $[MY]$ = concentration of the metal complex with Complexon-III
$[MI]$ = concentration of the metal complex with the indicator
$[Y^*]$ = sum of the concentration of the metal-free Complexon-III
$[I^*]$ = sum of the concentration of the metal-free indicator
K_Y^* = $[MY]/[M][Y^*]$ = apparent stability constant
K_I^* = $[MI]/[M][I^*]$ = apparent indicator constant

When the total concentrations of the metal and of the titrant in the system are m_t and c_t respectively, the following equation is obtained from eq. (2), so far as $m_t \geqq c_t$:

$$K=\frac{[I^*]}{[MI]}K_Y^*(m_t-c_t+[Y^*]) \qquad (3a)$$

Since in the present case $[Y^*]$ is so small that it can be neglected in the course of titration, eq. (3a) is converted into the following:

$$K=\frac{[I^*]}{[MI]}K_Y^*(m_t-c_t) \qquad (3b)$$

By transposing eq. (3b), comes the following equation:

$$c_t=-\frac{K}{K^*_Y}\frac{[MI]}{[I^*]}+m_t \qquad (4)$$

If the factor of titrant is n and the dilution of the solution by titrant can be neglected, there come the following relationships:

1) J. M. H. Fortuin, P. Karsten and H. L. Kies, *Anal. Chim. Acta*, **10**, 365 (1954).
2) T. Higuchi, C. Rehm and C. Barnstein, *Anal. Chem.*, **28**, 1506 (1956).
** In the following equations, ionic charges were omitted for convenience.

$$m_t = nV_{eq} \text{ and } c_t = nV \qquad (5)$$

where V_{eq} is the volume of titrant equivalent to the total amount of metal, m_t, and V is the volume of titrant added.

By substituting eq. (4) with eq. (5), comes the following equation:

$$V = -\frac{K}{nK^*_Y}\frac{[MI]}{[I^*]} + V_{eq} \qquad (6)$$

Values of $[MI]/[I^*]$ can be computed from the absorbancy readings by means of the following equation;

$$[MI]/[I^*] = (A_{S_I} - A_S)/(A_S - A_{S_{MI}}) \qquad (7)$$

where A_{S_I} =absorbancy of the metal free indicator

$A_{S_{MI}}$ =absorbancy of the metal-indicator complex

A_S =absorbancy during the course of titration

If $(A_{S_I} - A_S)/(A_S - A_{S_{MI}})$ is plotted against V, will result a straight line whose intercept on the V axis is equal to V_{eq}.

This is evident in Fig. 1 where the plot of $(A_{S_I} - A_S)/(A_S - A_{S_{MI}})$ vs. the volume of titrant is shown for the titration of magnesium with Complexon-III using EBT as indicator. About 50 ml. of the solution, which contained the definite amounts of magnesium sulfate, 2 ml. of 1 N ammonium chloride-ammonia buffer solution (pH 10) and 0.3 ml. of 0.5 % solution of EBT in ethanol, was titrated with 0.01 M solution of Complexon-III. Absorbancies 545 mμ were recorded at the beginning of the titration and at every 0.05 ml. of added titrant during the titration, until the minimum absorbancy was obtained. The photometric titration curve of the same titration as in Fig. 1 is shown in Fig. 2. Some of the results, obtained from the intercept as shown in Fig. 1, are given in Table I.

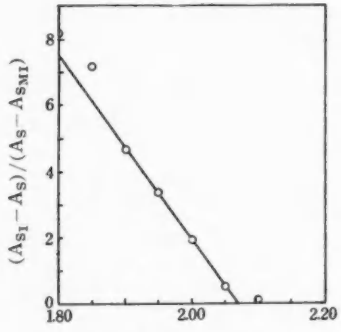


Fig. 1. Plot for titration of 0.504$_7$ mg. of Mg with Complexon-III using EBT indicator at pH 10.

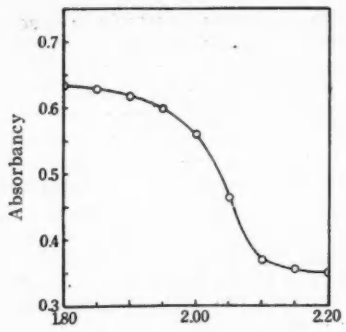


Fig. 2. Titration curve of the same titration as in Fig. 1.

TABLE I

RESULTS OF PHOTOMETRIC TITRATION OF MAGNESIUM WITH COMPLEXON-III USING EBT INDICATOR

Mg. taken, mg.	Titrimetric end point, ml.	Mg. found mg.	Error %
0.251_1	1.02_2	0.248_5	−1.0
0.251_1	1.04_5	0.254_1	+1.2
0.504_7	2.07_5	0.504_6	0.0
0.504_7	2.04_5	0.497_3	−1.5
0.504_7	2.07_0	0.503_4	−0.3
0.504_7	2.08_5	0.507_1	+0.5

Further studies on the characteristics of this plot and on its other applications will be reported in subsequent publications.

Department of Applied Chemistry
College of Engineering
University of Osaka Prefecture
Sakai, Osaka

Some Kinds of Reaction Behavior of Lucidusculine

By Takashi AMIYA

(Received July 18, 1957)

Some reactions concerning lucidusculine[1] (I), an alkaloid from *Aconitum luciduscul um Nakai*, have been investigated in this Laboratory. The methods are here communicated. Oxidation of I by 3% hydrogen peroxide gave lucidusculine N-oxide (II) d. p. 191°C (Found: C, 65.94; H, 8.37; H_2O, 3.31. Calcd. for $C_{24}H_{35}O_5N \cdot H_2O$: C, 66.18; H, 8.56; H_2O, 4.13%). Also oxidation of I by perbenzoic acid yielded a compound (III), d. p. 200°C, $[\alpha]_D^{15}$ −101° (CH_3OH) (Found: C, 65.30; H, 8.53%), identical (analysis, d. p. and methods of formation) with compound II. Reduction of III with zinc and hydrochloric acid regenerated substance I. Compound III afforded anhydrous compound (IV), when reserved in a desiccator, d. p. 205°C (Found; C, 69.32; H, 8.27. Calcd. for $C_{21}H_{35}O_5N$: C, 69.03; H, 8.45). Dehydration of III with 1% potassium chromate gave dehydrolucidusculine (V), m. p. 173—175°C (Found: C, 72.38; H, 8.75. Calcd. for $C_{21}H_{33}O_4N$: C, 72.15; H, 8.33%). Oxidation of I with N-bromosuccinimide gave a compound (VI), m. p. 175—180°C (Found: C, 71.51; H, 8.41%), identical (analysis and mixed m. p.) with compound V. Bromination of I with bromine in methanol gave bromoanhydrolucidusculine (VII), d. p. 210°C (Found: C, 50.02; H, 6.74; Br, 29.70; H_2O, 5.5. Calcd. for $C_{24}H_{32}O_3NBr \cdot HBr \cdot 2H_2O$: C, 49.73; H, 6.43; Br, 27.57; H_2O, 6.2%). The u. v. absorption of compound VII showed no λ max. at wavelengths 210–340 mμ. Oxidation of I with chromic anhydride in pyridine gave monocarboxylic acid (VIII), which showed neither definite m, p. nor definite d. p. (Found: C, 54.22, 54.60; H, 7.88, 7.69; N, 3.05. Calcd. for $C_{24}H_{31}O_5N \cdot 6H_2O$: C, 55.26; H, 8.31; N, 2.68%). In the infrared region the compound VIII showed a strong absorption near 5.85 μ, indicating the presence of the keto group. Methylation of VIII with diazomethan gave methyl ester (IX), which showed neither definite m. p. nor definite d. p. (Found: C, 57.01; H, 7.70. Calcd. for $C_{25}H_{33}O_5N \cdot 5H_2O$: C, 58.00; H, 8.37%). Because of its low yield and difficult purification, the analysis of IX led to only an approximate agreement. Since the presence of the terminal methylene group has already been confirmed[2] in I, the partformula of I may be tentatively summarized as,

$$C_{17}H_{20}\begin{cases} CH_2OH \\ OCOCH_3 \\ >CH(OH) \\ >N-C_2H_5 \\ >C=CH_2 \end{cases}$$

Further work is in progress and will be published later. The author is grateful to Professor Harusada Suginome, President of Hokkaido University, for his unfailing kindness in encouraging this work, and to Professor Shinichiro Fujise, Tohoku University, for his kindness in making the material available.

Department of Chemistry, Faculty of Science, Hokkaido University Sapporo

1) R. H. F. Manske and H. L. Holmes, "The Alkaloids", Vol. IV, Academic Press Inc., New York, (1954), p. 287.

2) T. Amiya and T. Shima, read before the 7th Annual Meeting of the Chemical Society of Japan held in Tokyo, April, 1954.

Diamagnetic Susceptibility of Zinc Oxide

By Yoshio MATSUNAGA

(Received May 24, 1957)

The reported values of specific diamagnetic susceptibility of zinc oxide are in poor agreement with each other. They include -0.29×10^{-6} and -0.43×10^{-6} by Hüttig et al.[1], -0.31×10^{-6} for the active oxide and -0.26×10^{-6} for the ignited sample by Turkevich and Selwood[2], and -0.3058×10^{-6} by Prasad et al.[3] It is well known that zinc oxide contains some kinds of lattice defect, namely cation and anion vacancies, besides an excess of zinc in interstitial positions, and their concentrations can be controlled by the type and the content of impurities. In the cases of zinc and cadmium sulfides, the diamagnetism was reported to depend on such variables. Therefore, measurements of

1) G. F. Hüttig, H. Radler and H. Kittel, *Z. Elektrochem.*, **38**, 442 (1932).

2) J. Turkevich and P. W. Selwood, *J. Am. Chem. Soc.*, **63**, 1077 (1941).

3) M. Prasad, S. S. Dharmatti and H. V. Amin, *Proc. Indian Acad. Sci.*, **26A**, 312 (1947), cf. *C. A.* **42**, 4410.

4) S. Larach and J. Turkevich, *Phys. Rev.*, **98**, 1015 (1955).

TABLE I
DIAMAGNETIC SUSCEPTIBILITY OF ZINC OXIDE
Addition (one mole per cent.)

	none	Al_2O_3	Ga_2O_3	Li_2O	Ag_2O	$ZnCl_2$
Low ignition	0.327	0.325	0.330	0.329	0.332	0.331
High ignition	0.333	0.329	0.335	0.336	0.330	0.331
Red	0.326					

magnetic susceptibilities of zinc oxides containing various impurities were undertaken for the purpose of examining the effects of lattice defects.

The slightly acidic solution of zinc sulfate was treated with metallic zinc to remove heavy metal ions. Ferrous iron was oxidized with hydrogen peroxide, and removed as the coprecipitate with zinc hydroxide by the addition of a small quantity of ammonium hydroxide solution. Then zinc oxalate was precipitated from the solution purified by the above mentioned methods, and calcined at 400°C for 6 hours. In the following section, we shall call the sample thus prepared zinc oxide (1). The samples containing Al_2O_3, Ga_2O_3, Li_2O, Ag_2O, and $ZnCl_2$ were prepared by the addition of definite amounts of solutions of the corresponding nitrates or $ZnCl_2$ to zinc oxide (1), The impregnated materials were dried at 110°C, and heated at 400°C for 6 hours (low ignition series) or at 900°C for 3 hours (high ignition series). Red zinc oxide was prepared by heating a mixture of zinc oxide (1) and ammonium nitrate (1:2) to the point of deflagration, and separated from residual ammonium nitrate and white zinc oxide by elutriation. According to Ehret and Greenstone[5], the amount of the excess of zinc in red zinc oxide prepared by this method is about 0.02 per cent.

The magnetic susceptibilities were measured using a Gouy balance as described in the previous paper[6]. The values multiplied by -10^6 are summarized in Table I. The susceptibility values of all samples are in accordance with one another within the limit of experimental error. Contrary to the results given by Turkevich and Selwood, diamagnetism seems to be rather great in the high ignition series. We could see the effects of impurities on the sintering of zinc oxide by the remarkable difference between their packing densities in a Gouy tube. For example, zinc oxide (1) was about twice as bulky as red zinc oxide and about 1.5 times as bulky as the samples containing Li_2O or Ag_2O in high ignition series. However, our magnetic data presented in Table I show conclusively the sintering and the type of impurities, consequently the kind and the concentration of lattice defects, do not appreciably affect the magnitude of the susceptibility of zinc oxide, and the disagreement between literature values can not be attributed to these variables.

The author wishes to express his hearty thanks to Professor H. Akamatu for his kind direction.

Department of Chemistry, Faculty of Science, The University of Tokyo
Hongo, Tokyo

5) W. Ehret and A. Greenstone, *J. Am. Chem. Soc.*, **65**, 872 (1943).
6) H. Akamatu and Y. Matsunaga, This Bulletin, **26**, 364 (1953).

On the Near Ultraviolet Absorption Bands of Disulfides

By Akira KUBOYAMA

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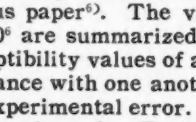
The alkyl disulfides whose two sulfur atoms adjoin each other, such as diethyl disulfide[1] (C_2H_5—S—S—C_2H_5) and cystine[1] show the longest wave length absorption maximum around 250 mμ ($\log\varepsilon\sim2.5$) in alcohol or water. But trimethylene disulfide[2] (TMD)  and its derivative, 6,8-thioctic acid[2] (α-lipoic acid) have an absorption maximum about 330mμ ($\log\varepsilon\sim2.2$) in 95% ethanol. This red-shift observed with cyclic disulfides is remarkable as compared with open chain disulfides (OCD) and will be treated in this communication. R. S. Mulliken[3] regarded the bands under consideration as due to

1) H. Ley and B. Arend, *Z. Phys. Chem.*, *B* **17**, 177 (1932).
2) R. B. Whitney and M. Calvin, *J. Chem. Phys.*, **23**. 1750 (1955).
3) R. S. Mulliken, *J. Chem. Phys.*, **3**, 506 (1953).

the electronic transitions, 3ps(nonbonding)→4ss*[1]. Here, probably 3p non-bonding orbitals are somewhat admixed with 3ss, but, now, as the first approximation this hybridisation is ignored. Briefly expressed by the molecular orbital method, 3ps and 4ss orbitals of disulfides split into $(3ps_1 \pm 3ps_2)$ and $(4ss_1 \pm 4ss_2)$, respectively, by the exchange intraction, and so the transition corresponding to the longest wavelength absorption is $(3ps_1 - 3ps_2) \rightarrow (4ss_1 + 4ss_2)$. According to this Mulliken's assignment, the above problem can be reasonably explained as follows. The S–S bond distances for TMD and OCD are assumed to be nearly equal. The energy of the upper molecular orbital $(4ss_1 + 4ss_2)$ may be considered nearly equal to each other for TMD and OCD, since the overlapping between $4ss_1$ and $4ss_2$ is almost invariant with the rotation around the S–S axis. So, this red-shift which corresponds to the transition energy diminution (ΔE_1), 1.20 eV., may be explained on the basis of the lower orbital $(3ps_1 - 3ps_2)$ energy. It may be thought that the mutual twist angle (θ) of the two C–S bonds around the S–S bond is nearly 90° for OCD, as for N,N-diglycyl-L-cystine dihydrate[4]. The situation is the same for dichlor disulfide[5], and hydrogen peroxide[6]. This is mainly due to the repulsive interaction between $3ps_1$ and $3ps_2$. On the other hand, the two C–S bonds of TMD are forced to take nearly cis-direction to each other around the S–S bond. By a molecular model, the maximum value of θ for TMD is ca. 40°. If θ for OCD and TMD are assumed to be 90° and 40°, respectively, the calculated overlap integral values (S) of $3ps_1$ and $3ps_2$ are zero and $(0.136 \times \cos 40° =) 0.103$. This means that in TMD the splitting between two orbital $(3ps_1 \pm 3ps_2)$ levels by the exchange interaction is much greater than that in OCD. Thus, the transition energy diminution can be qualitatively explained.

The fact that the OCD's 250 mμ bands are long-drawn-out absorptions is thought to be due to the change of θ-value caused by the thermal twisting vibration of the two C–S bonds around the S–S bond. In this connection, further comment will be made on the observed absorption specrum of hydrogen peroxide vapor[7]. This band with the continuously increasing intensity from 375 mμ to at least 215 mμ, may also be due to the transition, $(2po_1 - 2po_2) \rightarrow (3so_1 + 3so_2)$[3].

The rotational barrier height (ΔE_r) of the two C–S bonds around the S–S bond in disulfides can be roughly estimated from the above data. As is easily known from the above discussion, the energy (E_1) corresponding to the transition $(3ps_1 - 3ps_2) \rightarrow (4ss_1 + 4ss_2)$ and the total energy (E_2) of the four electrons of the two non-bonding orbitals $(3ps_1 \pm 3ps_2)$ are changeable with the angle θ. If we take OCD as the standard, the changes in these two quantities with θ can be represented by the following two formulae[8]:

$$\Delta E_1 = -(\beta - E_S S)/(1-S),$$

$$\Delta E_2 = 2\{(\beta - E_S S)/(1+S) - (\beta - E_S S)/(1-S)\}$$

where, β, E_S and S denote the resonance integrals, the energy of 3ps orbital and the overlap integrals, respectively. For the derivation of the above formulae, it is assumed that θ is 90° for OCD. From these two formulae the following simple relation can be derived:

$$\Delta E_2 = \Delta E_1 \times 4S/(1+S)$$

Under the assumption that the change in the total energy of non-bonding electrons (E_2) is the most important factor in determining ΔE_r and others such as the repulsive interaction between two alkyl groups and electrostatic interaction between C–S bonds can be neglected, ΔE_2 for $\theta = 0°$ roughly equals to ΔE_r. If further reasonable assumption that ΔE_1 is proportional to S which is proportional to $\cos\theta$ is used, ΔE_r equals $(1.20/\cos\theta_{TMD}) \times 0.544/1.136$ e.v.. Here, θ_{TMD} denotes θ in TMD. If θ_{TMD} is 40°, ΔE_r is 0.76 eV. This value is in good agreement with the one (0.74 eV.) obtained for dichlor disulfide by K. Hirota and T. Oka[5] from the wave number of the twisting vibration (106 $cm.^{-1}$).

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Faculty of Agriculture,
Miyazaki University.
Miyazaki

*1) In the following, subscription X denotes X atom
*2) Subscription S_1, S_2 denote the two sulfur atoms of disulfides.
4) H.L. Yakel and E. W. Hughes, *Acta Cryst.*, **7**, 291 (1954).
5) K. Hirota and T Oka, Presented at the Symposium on Structural Chemistry, Nagoya (1956).
6) J. T. Massey and D. R. Bianco, *J. Chem. Phys.*, 22, 442 (1954).
*3) The overlap intehral values were obtained by Mulliken et al's table, *J. Chem. Phys.*, **17**, 1248 (1949), assuming the atomic distance to be 2.04A; D.P. Stevenson and J. Y. Beach, *J. Am. Chem. Soc.*, **60**, 2872 (1938).
*4) S for $\theta = 0°$ is 0.136.
7) H. C. Urey, L. H. Dawsey and F. O. Rice, *J. Am. Chem. Soc.*, **51**, 1371 (1929).
8) C. A. Coulson, "Valence". Oxford (1952) p. 78.

*An X-Ray Study on the Crystal Structure of 2-Chloro-2, 3, 3-trimethylbutane**

By Tsutomu KOIDE, Satoshi TAKEUCHI, Tsutomu ODA, Yasusada YAMADA** and Inao TAGUCHI**

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Crystals of hexamethylethane undergo phase transition at −125°C.[1] The phase between the transition and the melting point (m. p. 100.6°C) is characterized by the softness and the high volatility. The crystal structure was investigated by West,[2] who vaguely pointed out that the molecules in the crystal are in orientational or rotational disorder. In order to see what will occur in the high temperature modification by replacement of a methyl group by chlorine, we have carried out an X-ray examination of 2-chloro-2, 3, 3-trimethylbutane, which has relatively high melting point, 134–135°C.[3]

Following the method used by Butlerow,[3] we prepared 2-chloro-2, 3, 3-trimethylbutane by adding powder of phosphorus pentachloride to pentamethylethanol hydrate, which had been obtained by the Grignard reaction[4] of pinacolone with methyl magnesium bromide in ether. The final product, $Cl(CH_3)_2C-C(CH_3)_3$ was recrystallized from its ethereal solution and then subjected to sublimation under low pressure.

It was observed that the solid sealed in a thin-walled melting point tube melts at 134–135°C. It recrystallizes readily in a closed vessel to give transparent aggregates. The solid is very soft and plastic. We have found it to be optically isotropic. The vapor has a camphoric odor. These properties are similar to those of cubic hexamethylethane. By the suspension method in the dilute aqueous solution of sodium chloride, the density of the solid was determined as 0.999 g./cc. at 15°C.

As the solid is volatile, we used single crystals sealed in thin-walled glass capillary tubes for X-ray examination. Such a sample was placed on a goniometer-head of an X-ray camera. Using Cu-radiations, we took several Laue photographs and a series of 20° oscillation photographs over a range of 75° about [001] as the axis of rotation. Laue photographs taken with the X-ray beam parallel to [100] and [110] showed holotesseral symmetry, and thus the point group of the crystal should be $T_d-\bar{4}3m$, $O-43$ or O_h-m3m. All reflections appearing on the oscillation photographs were indexed satisfactorily by a cubic reciprocal lattice corresponding to $a=7.62$ Å. All spots were extinguished except those for which $h+k+l=2n$. This indicates that the lattice is of the body-centered cubic. Thus the space group should be $T_d^3-I\bar{4}3m$, O^5-I43 or O_h^9-Im3m. The density indicates two molecules per unit cell, the densities being calculated, 1.01 g./cc.; observed, 0.999 as mentioned above.

Since there are two molecules in the unit cell with the body-centered translation, it is reasonable to place the centers of molecules at the positions 0, 0, 0 and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, of which the symmetry should be $T_d-\bar{4}3m$, $O-43$ or O_h-m3m. On the other hand, as the rigid molecule of $(CH_3)_2ClC-C(CH_3)_3$ can have at the highest only one plane of symmetry C_s-m, which contains the central C—C bond axis, it becomes necessary to consider some statistical explanation of the structure, as is always so[2,5] in organic plastic crystals. In order that the statistical symmetry of the molecule be as high as $T_d-\bar{4}3m$ at 0, 0, 0 and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, the molecule should orientate its central C—C bond axis parallel to each one of the four body-diagonals statistically equally and at the same time laterally so that the C—C axis acquires a statistical symmetry $3m$ at least. Such a statistical symmetry can also be gained by a model of molecules in rotation about the C—C axis. In the cases of O^5-I43 and O_h^9-Im3m, it is necessary to add the anti-parallel orientations of the polar C—C axis along the four body-diagonals, these directions having the symmetry of 3 or $3m$. It is also conceivable that the observed feature of the X-ray diffraction can be explained by assuming molecules in free spherical rotation. Which one of

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** Faculty of Science, Osaka University, Nakanoshima, Osaka.

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2) C. D. West, *Z. Krist.*, **88**, 195 (1934).
3) H. A. Butlerow, *Ann.*, **177**, 183 (1875).
4) L. Henry, *Chem. Zentr.*, II, 748 (1906).
5) I. Nitta and T. Watanabé, This Bulletin, **13**, 28 (1938); T. Oda and T. Watanabé, *J. Chem. Soc. Japan*, **65**, 154 (1944). See also T. Oda, *Memoirs of the Osaka University of the Liberal Arts and Education*, B, No. 2, 1 (1953); R. S. Schwartz, B. Post and I. Fankuchen, *J. Am. Chem. Soc.*, **73**, 4490, 5113 (1951); H. J. Backer and W. G. Perdok, *Rec. trav. chim.*, **62**, 533 (1943).

these possibilities is the case for the actual statistical structure seems indiscernible from the consideration of intensity data, since the observable reflections are few. However, it may be said that the structure found for the present crystal is statistically isomorphous with that of the high temperature modification of $C_2(CH_3)_6$[2].

The rapid decrease in intensity of the X-ray reflections with increasing angle of scattering is evidently due to the disordered orientation of molecules with violent thermal motion. In accordance with these X-ray observations, the crystal is soft, plastic and highly volatile.

With a view that such a "rotational" mode of the molecules in crystals will cease at lower temperatures, we have undertaken a differential thermal analysis, and observed an anomalous heat effect at about −146°C on cooling, and at about −139°C on heating, showing hysteresis phenomenon. We have also taken X-ray oscillation photographs at about −160°C, which give a number of reflections showing that the structure below the thermal transition point is of low symmetry and probably has a more ordered structure.

In conclusion, we desire to express our hearty appreciation to Professor Isamu Nitta, Professor Tokunosuké Watanabé and Dr. Shuzo Seki, Faculty of Science, Osaka University, for their interest during this work. The cost of this research was defrayed from the Scientific Research Grant from the Ministry of Education, to which the thanks of the present authors are due.

Chemical Laboratory, Osaka University of Liberal Arts and Education
Tennoji, Osaka
Faculty of Science, Osaka University
Nakanoshima, Osaka